Atmospheric Effects of Aviation: First Report of the Subsonic Assessment Project

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Introduction and Overview

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BACKGROUND

A number of scientific studies have suggested that cruise level emissions from aviation may contribute to detrimental chemical changes in the global atmosphere (i.e., particularly ozone content), as well as other climate modifications. The most widely accepted assessments are those conducted by United Nations (UN) scientific organizations. Ozone trends are assessed by the United Nations Environment Programme (UNEP) and the World Meteorological Organization (WMO). Their latest assessment [WMO, 1995] is that:

> Estimates indicate that present subsonic aircraft operations may have increased NO_x concentrations at upper tropospheric altitudes in the North Atlantic flight corridor by about 10-100%, water vapor concentrations by about 0.1% or less, SO_x by about 10% or less, and soot by about 10% compared with the atmosphere in the absence of aircraft and assuming all aircraft are flying below the tropopause.

> Preliminary model results indicate that the current subsonic fleet produces upper tropospheric ozone increases as much as several percent, maximizing at the latitudes of the North Atlantic flight corridor.

> The results of these rather complex models depend critically on NO_x chemistry. Since there are large uncertainties in the present knowledge of the tropospheric NO_x budget (especially in the upper troposphere), little confidence should be put in these quantitative model results of subsonic aircraft effects on the atmosphere.

And finally:

> Early assessments of the impact of aircraft on the stratosphere varied enormously with time as understanding slowly improved. Our understanding of the lower stratosphere/upper troposphere is still far from complete and surprises can still be anticipated, which may either result in greater or lesser aircraft effects of the atmosphere.

The analogous current assessment of aviation's possible climate impact comes from the Intergovernmental Panel on Climate Change [IPCC, 1995] which reports that:

> Aircraft release NO_x directly into the free troposphere. Such emissions could increase ozone concentrations at altitudes where ozone is at its most effective as a greenhouse gas. The radiative forcing resulting from such emissions could thus be more important than equivalent NO_x emissions at the surface. Until the various contributions to NO_x and O_3 levels in the free troposphere can be better quantified, the relative importance of the various NO_x sources in perturbing O_3 amounts cannot be reliably estimated. However, reasonable upper limits may be placed on the radiative forcing due to increased O_3 produced by the NO_x relative to that from the CO_2 emitted by aircraft. Aircraft emit about 3% of total CO_2 emissions from fossil fuel combustion and a similar fraction of anthropogenic

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NO_x. Our current best estimate is that the positive radiative forcing due to the release of NO_x from aircraft could be of similar magnitude or smaller than the effect of CO_2 released from aircraft. These estimates are preliminary and may well change in future assessments.

Aircraft also emit carbon monoxide, water vapor, soot and other particles, sulfur gases and other trace constituents which have the potential to cause radiative forcing. The impact of such emissions has not yet been properly assessed.

These scientific cautions about the possible impact of aircraft emissions on the global environment have, in turn, resulted in concerns raised by influential public interest organizations. For example, the Environmental Defense Fund [Vedantham and Oppenheimer, 1994] has recently stated that:

Scientific research on the environmental effects of aviation must be accelerated ...
Nevertheless, proactively limiting aviation emissions now will reduce the risk to the global environment, while allowing more flexibility later in managing all sources of climate change and ozone depletion.

The World Wide Fund for Nature (aka World Wildlife Fund) [Barrett, 1994] has recommended even more severe restraints on aviation:

... if policies remain unchanged, pollution from aircraft will double in the next two decades or so. A series of new or improved policy measures is therefore needed ... demand management will be necessary.

Because of the considerable uncertainty about aviation's impact on the atmosphere, it is difficult to respond to these proposals for somehow limiting aircraft emissions, but clearly there is also enough scientific concern to warrant continued study. And the Committee on Aviation Environmental Protection [CAEP, 1992] of the International Civil Aviation Organization has already begun consideration of related regulatory standards for high-altitude emissions.

In response, focused studies of the atmospheric impact of aviation have begun in Europe [Schumann and Wurzel, 1994] and elsewhere based on the scientific concerns and regulatory considerations. An American governmental review [OTA, 1994] led to the formulation of the Subsonic Assessment (SASS) Project as an element of the NASA Advanced Subsonic Technology Program (ASTP) to:

• Participate constructively in related ongoing UN ozone and climate assessments.

• Address concerns raised by independent scientific studies.

• Ensure that interests of American aviation are fairly represented in regulatory considerations.

NASA's leadership in aeronautical science is well known, beginning in 1915 with its predecessor agency, the National Advisory Committee for Aeronautics. In response to a more recent

Congressional mandate, programs have been developed in the NASA Office of Mission to Planet Earth (MTPE) to undertake research and monitoring of the Earth's upper atmosphere, and to assess the related state of knowledge with respect to natural and human-induced changes. That effort has utilized a focused approach coupled with an open, competitive, peer-review process that selects the best scientific efforts aimed at addressing the identified issues, and coordinates the research with regular international scientific assessments of the state of knowledge of the upper atmosphere. The research has provided the scientific basis for the precedent-setting international protocols regulating ozone-depleting substances, and is well respected by all communities: scientific, policy, environmental, and industry.

Following that model, the NASA Office of Aeronautics has collaborated with MTPE since Fiscal Year (FY)1990 in assessing the possible atmospheric impact of future supersonic aircraft [NASA 1993; NRC, 1994; Stolarski *et al.*, 1995]. That Atmospheric Effects of Stratospheric Aircraft (AESA) element of the NASA High-Speed Research Program (HSRP) was joined with SASS in FY 1994 to form the single Atmospheric Effects of Aviation Project (AEAP). In the first year of the new effort, SASS supported research that augments ongoing NASA aeronautical and atmospheric science programs and focuses them on new areas appropriate for subsonic aviation. An expanded long term effort has been implemented through a NASA Research Announcement (NRA) that more keenly focuses on the subsonic aviation questions. NRAs will be issued on an approximately three-year cycle to renew investigators' participation in SASS and to further develop the research program.

The subsonic assessment task is enormously complex and guiding principles for SASS acknowledge time and resource limitations. Given present knowledge of the atmosphere, the technology of observations, and the status of global modeling, it is clear that "complete answers" may be beyond the extent of SASS. Still, the scientific community has maturing tools (i.e., instruments and models) and greater assessment experience than when AEAP began. Therefore, solid progress and good answers to a few well-posed questions are expected from SASS prior to its planned completion in FY 2001; and useful guidance should be available to assist policy considerations. In recognition of that goal, the Federal Aviation Administration has joined AEAP as a partner via Interagency Agreement.

TECHNICAL APPROACH

Scientific Issues

At cruise altitude, most emissions from current civil jet aircraft are deposited in well-traveled transcontinental or transoceanic corridors, located in the lower stratosphere or upper troposphere (i.e., about 8 to 12 km altitude), depending on tropopause height. The exception is the current (small) supersonic fleet which has a cruise altitude of ~16 km. We note that the term "subsonic assessment" (or "SASS") as used in this report includes the currently operating supersonic aircraft. Related major problems posed to SASS are summarized schematically in Figures 1-1 and 1-2, with two areas of concern illustrated. The first issue is whether subsonic emissions affect ozone in the upper troposphere and lower stratosphere (UT/LS). The second issue is whether emissions of water (H_2O), sulfur dioxide (SO_2), and soot, which can lead to contrail and

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$\overline{O + O_3 \rightarrow O_2 + O_2}$$

$$NO_2 + h\nu \rightarrow O + NO$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$OH + CO \rightarrow H + CO_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$\overline{CO + 2O_2 + h\nu \rightarrow CO_2 + O_3}$$

Mid-Latitude Model

Altitude (Kilometers)

40
30
20
10
0

Deplete Ozone

Mach 3.2
Mach 2.4
Mach 2.0

Subsonic Fleet

Enhance Ozone

0   0.2   0.4

Concentration (mg/m³)
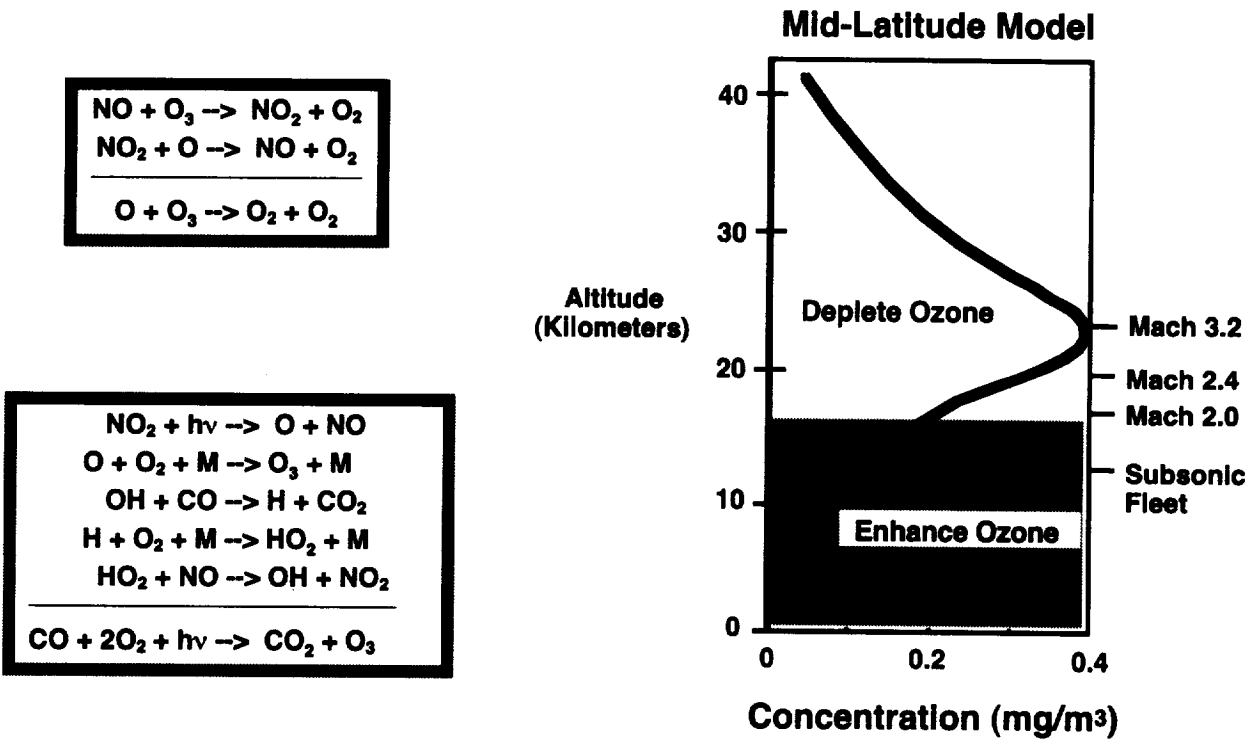
Figure 1-1. Effects of NO_x emissions on ozone.

*CFC
*N₂O
*CH₄

NO_x → *O₃

Sun

HC

*CO₂

Clouds

Soot (C)
*H₂O
SO₂

*Greenhouse Gases

Condensation Nuclei

Temperature
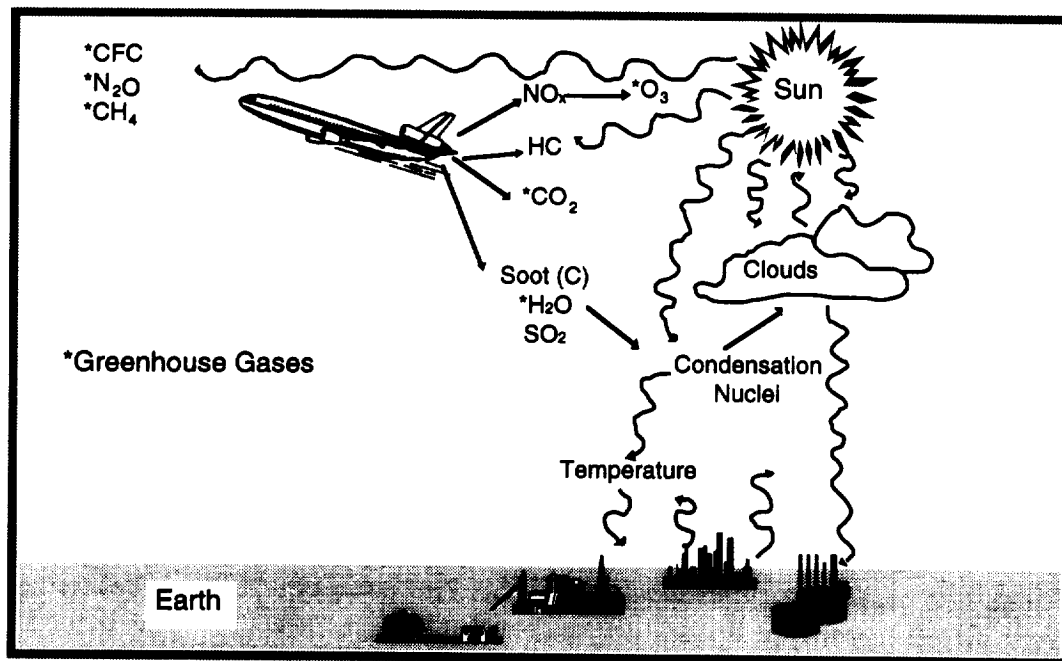
Earth

Figure 1-2. Climate effects of emissions.

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aerosol formation, modify atmospheric water content, cloudiness, and aerosol characteristics to perturb radiative properties of the UT/LS. Obviously, the distinction between "chemical" and "radiative" consequences of emissions is somewhat artificial. For example, ozone is a greenhouse gas, and related chemical changes result in radiative processes and dynamical effects.

Thus, the overall objective of SASS is to develop an assessment that can answer these questions for the current and future civil aviation fleet:

- How do aircraft emissions (e.g., nitrogen oxides (NO_x), sulfur oxides (SO_x), H_2O, carbon monoxide (CO), hydrocarbons, soot, and carbon dioxide (CO_2)) and their subsequent products (ozone, aerosols) affect radiative forcing and climate?

- How do aircraft emissions affect ozone in the UT/LS and total column?

Technical Strategy

The primary SASS objective focuses on prediction of the current and future atmospheric effects of aviation. In pursuing this objective the program seeks to build on the progress made by existing tropospheric and stratospheric research programs in the areas of atmospheric concepts, model formulations, and instrument technology. SASS efforts are intended to:

- Promote advancements in the conceptual understanding of UT/LS processes and aircraft wake and plume processes.

- Facilitate improvements in computational model representations of the global atmosphere, the UT/LS, and aircraft plumes.

- Improve input databases for models, specifically those for aircraft operational scenarios, photolysis rates, chemical reaction rates, and source gas emissions from the Earth's surface.

- Denote and quantify, where possible, uncertainties in the conceptual understanding and model representation of atmospheric processes related to aircraft impacts.

Strategic Implementation Plan

A simplified schematic of the SASS strategic implementation plan is shown in Figure 1-3. SASS milestones are summarized in Table 1-1. Early work emphasizes collection of existing observational databases, assembly of realistic emission databases for the current subsonic fleet, and construction of a rigorously verifiable three-dimensional (3-D) chemistry and transport model. This will be followed by research directed at improving the understanding of the relationships between aircraft particulate exhaust and atmospheric radiative forcing, aircraft nitrogen oxide emissions and ozone photochemistry, and atmospheric transport and dispersal of aircraft exhaust. All of the subsequent research will be folded into improved model representations. It should be noted that results from the first two campaigns could influence the direction of the latter campaigns.

| FY 1994 | FY 1995 | FY 1996 | FY 1997 | FY 1998 | FY 1999 | FY 2000 | FY 2001 | FY 2002 |
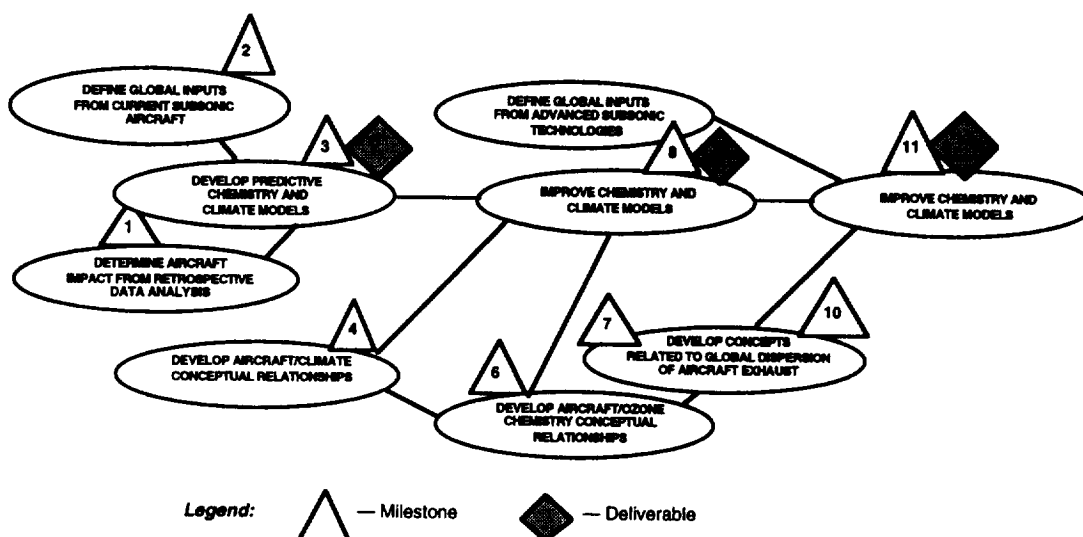
Figure 1-3. Schematic of SASS strategic implementation plan.

Table 1-1. SASS milestones.

Milestones	Qtr	FY
1. Collect available observational data pertinent to understanding long term changes (i.e., climatology) of reactive nitrogen (NO_y) in lower atmosphere	4	1994
2. Characterization of emissions from current technology engines	4	1995
3. Complete application of computer models in support of assessment report	3	1996
4. First SASS-sponsored field campaign with DC-8 Flying Laboratory – climate related measurements. [SUCCESS (SUbsonic aircraft Contrail & Cloud Effects Special Study)]	4	1996
5. First program-level assessment report, leading to participation by principal investigators in preparation of 1997 UNEP/WMO ozone assessment report	4	
6. Second SASS-sponsored field campaign with DC-8 Flying Laboratory – nitrogen and ozone chemistry-related measurements	4	1997
7. Third SASS-sponsored field campaign with DC-8 Flying Laboratory – tropical convection-related measurements (preliminary plan)	4	1998
8. Complete application of computer models in support of assessment reports	3	1999
9. Second program-level assessment report, leading to participation by principal investigators in preparation of 2000 UNEP/WMO ozone and IPCC climate assessment reports	4	
10. Fourth SASS-sponsored field campaign with DC-8 Flying Laboratory – lightning observations (preliminary plan)	4	2000
11. Complete application of computer models in support of assessment reports	3	2001
12. Final program-level assessment report	4	2001

Embedded in this general plan are a complex array of narrowly focused research activities. Organization and management of these activities is enhanced by subdividing the overall effort into six subelements, three of which are unique to the aviation aspect of the assessment (Emissions Characterization, Near Field Interactions, and Operational Scenarios), and three of which are associated with contemporary atmospheric science (Laboratory Studies, Atmospheric Observations, and Global Modeling). The first three subelements encompass activities designed to define the global inputs from present and future subsonic aircraft. These global-scale emissions will be used as input into assessment models developed within the Global Modeling subelement. Development of the assessment models will be based on progress in the understanding of the atmosphere's response to aircraft emissions. Refinement of atmospheric chemistry, transport, and radiation process models will be achieved within the Atmospheric Observations and Laboratory Studies subelements.

As part of the implementation plan, specific questions have been posed for each program subelement. Table 1-2 summarizes these questions and the planned approach to answering the research questions.

PROGRAM PROGRESS AND CURRENT STATUS

The first year of SASS (FY94) consisted of two primary activities:

(1) Preliminary, one-year only, studies by investigators in existing NASA research programs whose research is directly related to SASS objectives. This "fast-SASS" selection was conducted in coordination with NASA MTPE Program Managers. Letter proposals were reviewed from 44 investigators in the AESA, Upper Atmosphere Research Program (UARP), Atmospheric Chemistry Modeling and Analysis Program (ACMAP), and Tropospheric Chemistry, and Radiation Sciences Programs. The principal activities funded were analysis of existing data to search for the subsonic aircraft signal, supplementing Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) data analysis for information on atmospheric transport, data archiving for comparison with models, preliminary model calculations of subsonic effects, and instrument development to improve capabilities for SASS Observations. The fast-SASS investigators are listed in Table A-1 in Appendix A; their research summaries appear in Appendix B.

(2) Detailed Program formulation was conducted through a series of workshops, and competitive investigator selections were made through an NRA (see Table 1-3). Selections of Investigators were made over a period of three months which included mail reviews, prioritization meetings with NASA MTPE Program Mangers, SASS subelement managers, and the AEAP Advisory Panel in March 1994. Of the 160 proposals reviewed, 60 were selected, including 5 from non-U.S. Principal Investigators (PIs).

Proposal selection was made and funding was issued toward the end of FY94. Typically, the proposals covered a three-year effort. Research summaries (see Appendix B) were prepared in spring 1995 and thus represent the first year of SASS. The 3-D Global Modeling Initiative

Table 1-2. Summary of scientific questions and programmatic responses.

Aviation-Unique Topics

Emissions Characterization

Question:	What are emissions constituents for current and future commercial jet engines?
Program Response:	Develop diagnostic measurements from ongoing efforts; define combustor and engine exhaust (NO_x, HC, CO, soot, and H_2O) for existing technology, and for advanced, low-NO_x technology being developed in the ASTP and HSRP.

Near-Field Interactions

Question:	Can fluid dynamics and/or chemical processes in aircraft wakes alter properties of engine exhaust products or their deposition altitude to significantly influence the background atmosphere?
Program Response:	• Develop efficient and accurate algorithms for thermodynamic, physical, and chemical properties of wake and exhaust products between the engine exhaust plane and the location where interaction is influenced only by background atmosphere.
	• Couple models with *in situ* and/or remote exhaust plume measurements using current aircraft platforms.

Operational Scenarios

Question:	What are current and future emissions from aircraft?
Program Response:	Develop and maintain a 3-D (i.e., altitude, latitude, and longitude) database representing total aircraft emissions along realistic flight paths for past, current, and future operations.

Atmospheric Science Topics

Laboratory Studies

Question:	What chemical and physical processes in the atmosphere could be perturbed by aircraft emissions?
Program Response:	• Use model sensitivity studies to identify chemical and radiative processes most likely to be perturbed or, in collaboration with models, place upper limits on minor processes.
	• Identify chemical processes for gas, liquid, and solid phases that are affected by aircraft emissions.
	• Determine rates of physical and chemical processes to guide observations and modeling.

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Table 1-2 (continued). Summary of scientific questions and programmatic responses.

Atmospheric Observations - Chemistry

Questions:
- What is NO_x conversion time and odd nitrogen partitioning in lower stratosphere and upper troposphere?
- What is aircraft contribution to upper troposphere NO_x budget compared to strat/trop exchange, lightning, and convective input of pollution?
- How reliably can NO_x and NO_y (gas and bulk phase) be measured in the upper troposphere and how does it affect the reliability of a NO_x budget assessment?

Program Response:
- Perform *in situ* measurements of tracers (e.g., CO_2, N_2O, CH_4).
- Plan NO_x and HO_x budget experiment(s).
- Support development work on NO_x and NO_y sensors.
- Assemble existing NO_x and NO_y database and study budget information from past UT/LS measurement campaigns.

Atmospheric Observations - Radiative Processes

Questions:
- What are effects of contrails on Earth's radiation budget?
- Does aircraft exhaust affect ambient cirrus properties?
- Do aircraft emit enough soot or sulfate to be radiatively significant?

Program Response:
- Satellites and ground based observations, supplemented by aircraft overflights.
- Focused aircraft expedition to sample ambient clouds, including chemical composition.
- Retrospective analyses of aerosol data, use of estimated emissions from aircraft, and future measurements.

Global Modeling

Questions:
- What are predicted ozone changes and climatic impact associated with aviation?
- Can models explain observations?
- What are uncertainties in these predictions?

Program Response:
- Develop 3-D global chemical transport assessment model
- Use global climate models and their embedded radiative models to evaluate the potential climate forcing from aircraft.
- Test models against atmospheric measurements.
- Model intercomparisons and error analysis, including subgrid processes and parameterizations.

Table 1-3. SASS-related workshops and NRA schedule.

Date	Activity	Location	Workshop Chair
April 1993	Kickoff Workshop - Chemistry/Dynamics Issues	Alexandria, VA	A. Thompson
July 1993	Kickoff Workshop - Radiation Issues	Washington, DC	A. Thompson
October 1993	NRA for SASS proposals distributed	n/a	n/a
November 1993	Heterogeneous Chemistry Workshop	Boulder, CO	A. Ravishankara
November 1993	Engine Exhaust and Trace Chemistry Committee Meeting	Billerica, MA	F. Dryer
December 1993	NO_y Workshop	Menlo Park, CA	D. Crosley
December 1993	Deadline for SASS NRA proposals	n/a	n/a
January 1994	SASS Aircraft Mission Measurement Strategies Workshop	Boulder, CO	D. Baumgardner
January 1994	SASS NRA proposal prioritization	Washington, DC	n/a
February 1994	USAF Coordination Meeting	Washington, DC	H. Wesoky
February 1994	Commercial Aviation Applications Meeting	Washington, DC	A. Schmeltekopf
March 1994	SASS Program Plan development	n/a	n/a
March 1994	SASS NRA proposal selection	Satellite Beach, FL	A. Thompson
May 1994	SASS Data Needs Workshop	Washington, DC	W. DeMore
June 1994	SUCCESS Experiment Planning Meeting	Moffett Field, CA	O. Toon
June 1994	Kickoff Workshop - 3-D Global Modeling Initiative	Washington, DC	J. Rodriguez
September 1994	3-D Global Modeling Initiative letter proposals due	n/a	n/a
December 1994	3-D Global Modeling Initiative Science Team Meeting	Pleasanton, CA	J. Rodriguez and D. Rotman

(GMI), was formulated in summer 1994 as a jointly sponsored activity of SASS and AESA Phase II. This activity was well underway by the end of the calendar year 1994.

The present status of SASS can be summarized as follows.

- On-schedule progress towards an interim Program Assessment for late 1996. A Global Modeling strategy has been adopted to meet this schedule that includes model intercomparisons of chemical mechanisms and solutions, model calculations to evaluate global transport of NO_x, definition of databases of atmospheric observations for testing models, sensitivity studies, and climate impact studies.

- On-schedule construction of a central or "core" 3-D chemistry and transport model for assessment scenario runs. The model is being assembled from a number of state-of-the-art subroutines prepared by investigators who are part of the core model science team.

- One major SASS field campaign (SUbsonic aircraft: Contrail and Cloud Effects Special Study (SUCCESS), co-sponsored by the First ISCCP (International Satellite Cloud Climatology Project) Regional Experiment (FIRE) activity within the Radiation Sciences Program of the Office of Mission to Planet Earth), directed at relating particle microphysical properties with the corresponding radiative properties is scheduled for April/May 1996.

- One near-field interaction mini-experiment, the SASS Near-Field Interaction Flight Experiment (SNIF), directed at aircraft wake dynamics particle evolution, and acid formation is scheduled for early 1996. In addition, extensive ground-based lidar measurements of fluid mechanics and some flight measurements of chemistry have been performed at the NASA Langley Research Center.

- SASS is providing support for the ongoing Stratospheric Tracers of Atmospheric Transport (STRAT) aircraft missions, jointly sponsored by AEAP and UARP, that will give interim answers on critical SASS issues of tropospheric and stratospheric residence times.

- Some tasks in preparation for a major 1997 chemistry-oriented aircraft mission have been completed and some instruments critical to the mission aims (i.e., hydroxyl radicals (OH), nitrogen dioxide (NO_2), and nitric acid (HNO_3)) are under development. This campaign will probably be coordinated with STRAT, the AESA/UARP Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) aircraft campaign and, it is hoped, with field campaigns conducted by other U.S. agencies and non-U.S. Programs.

- Strategies for using commercial/military platforms to build climatology for a limited set of species have been considered (Section 7.3) but not yet implemented.

- Exhaust characterization sampling techniques have been successfully developed and utilized in an advanced military engine test conducted in October 1995 (Chapter 3).

- A number of small, single investigator research tasks aimed at conducting retrospective analysis of existing databases, providing laboratory data on atmospheric chemical reactions, and producing models of aircraft plume dynamics and chemistry are underway.

The chapters in this report give highlights or background in each of the Program subelements discussed above.

ACKNOWLEDGMENTS

We gratefully acknowledge the work of the scientists who authored and reviewed these chapters. The principal authors and contributors are listed on each chapter, and the reviewers are given in Appendix E. The efforts of Cindy Alami, Rose Kendall, and Kathy Wolfe of Computer Sciences Corporation were essential in the editing and preparation of this document.

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Chapter 2

Subsonic Aircraft Emission Inventories

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INTRODUCTION

In order to evaluate the effects of aircraft emissions on the atmosphere, it is necessary to develop inventories of the emissions as a function of geographical position. Detailed inventories which account for scheduled, charter, military, and former USSR air traffic have been developed for 1990 and projected to 2015. [Wuebbles *et al.*, 1993; Baughcum *et al.*, 1994; Landau *et al.*, 1994]. These studies have taken a "bottoms-up" approach in which aircraft schedules are utilized, the aircraft/engine combinations are identified, and then detailed calculations of fuel burned and emissions are done along each flight path. Other studies have used a mixture of a "bottoms-up" approach to account for scheduled air traffic and a "top-down" approach to account for military and non-scheduled traffic [McInnes and Walker, 1992; Schumann, 1995].

In this chapter, we provide a brief overview of the basic approach used in the development of aircraft emission inventories for the NASA studies and the results obtained to date. We note that the term "subsonic" includes the small fleet of currently operating supersonic aircraft.

AIRCRAFT EMISSION CHARACTERISTICS

Emission characteristics for proposed advanced supersonic aircraft have been reviewed earlier [Miake-Lye *et al.*, 1992]. Aircraft emissions basically fall into two categories: those determined by fuel properties and those determined by engine design.

The primary emissions are carbon dioxide (CO_2) and water vapor (H_2O) produced by the combustion of jet fuel. The emission levels are determined by the fuel consumption and the fraction of hydrogen and carbon contained in the fuel. Results from a Boeing study of jet fuel properties measured from samples taken from airports around the world yielded an average hydrogen content of 13.8% [Hadaller and Momenthy, 1989]. Similarly, emissions of sulfur dioxide (SO_2) from aircraft engines are determined by the levels of sulfur in the jet fuel. Jet fuel specifications require sulfur levels below 0.3% but levels are typically much lower than this. The Boeing measurements obtained an average sulfur content of 0.042% with 90% of the samples below 0.1% [Hadaller and Momenthy, 1989]. Future sulfur levels are projected to drop to about 0.02% [Hadaller and Momenthy, 1993].

The emissions are characterized in terms of an emission index (EI) in units of grams of emission per kilogram of fuel burned. Current and projected EIs (in units of grams of emissions per kilogram of fuel burned) are summarized in Table 2-1, based on the analyses of Hadaller and Momenthy for commercial Jet A fuel.

Nitrogen oxides (NO_x), carbon monoxide (CO), and hydrocarbons are produced within the combustors and vary in quantity according to the combustor conditions. Nitrogen oxides are produced in the high-temperature regions of the combustor primarily through the oxidation of atmospheric nitrogen. Thus, the NO_x produced by an aircraft engine is sensitive to the pressure, temperature, flow rate, and geometry of the combustor. The emissions vary with the engine power setting, being greatest at high-thrust conditions. By contrast, CO and hydrocarbon emissions are highest at low power settings where the engine temperature is low and combustion is less efficient.

Table 2-1. Recommended emission indices in units of grams emission/kilogram fuel for 1990 and projected to 2015.

Emission Index (EI)	1990	2015
Carbon Dioxide (CO_2)	3155	3155
Water (H_2O)	1237	1237
Sulfur Oxides (as sulfur dioxide, SO_2)	0.8	0.4

Nitrogen oxides consist of both nitric oxide (NO) and nitrogen dioxide (NO_2). For NO_x, the emission index (EI_{NO_x}) is given as gram equivalent NO_2 to avoid ambiguity. Although hydrocarbon (HC) measurements of aircraft emissions by species have been made [Spicer et al., 1992], only total hydrocarbon emissions are considered in this work, with EI_{HC} given as equivalent methane (CH_4).

As part of the certification process for each commercial aircraft engine type, NO_x, HC, and CO emissions are measured on engine test stands and corrected to standard day, sea level conditions. Measurements are made at power settings of 7% (idle), 30% (approach), 85% (climb out), and 100% (take-off). These measurements have been developed to evaluate aircraft emissions in the vicinity of airports, rather than for cruise altitude conditions. They do, however, provide a comprehensive database for interpolation to cruise conditions.

In Figure 2-1, typical data available from the International Civil Aviation Organization (ICAO) database [ICAO, 1995] is illustrated for two engines which are used on the Boeing 747. The NO_x EI increases monotonically with power setting, while both the CO and hydrocarbon EIs decrease by 1 to 2 orders of magnitude as fuel flow increases. This figure also illustrates the dramatic improvements that have been made in CO and hydrocarbon emissions with the introduction of more efficient engines. The PW4056 was certified in 1986 while the JT9D-7F was certified in 1975. It is important to emphasize that the data shown are for sea level conditions and do not correspond to cruise altitudes. For cruise conditions, corrections for both installation effects and ambient conditions must be included.

Empirical relationships have been developed by the engine manufacturers which relate EIs to combustor inlet temperatures (T_3) and pressures (P_3), at both standard day and ambient conditions [Lyon et al., 1979; 1980]. Using these relationships, the complete thermodynamic cycle for a specific engine type can be used to explicitly calculate the EIs at different operating conditions. Such detailed data of the engine performance are proprietary to the engine manufacturers.

For the calculation of a global inventory of aircraft emissions, a thermodynamic cycle analysis would be impractical, both in terms of computer resources and engineering manpower. Methodologies have been developed for calculating the EIs at different flight conditions and altitudes using correlations between the measured EIs from ground tests and the fuel flow rate [Martin, Zeeben, and Oncina, private communication; Baughcum et al., 1994; 1996]. The Boeing method developed by Zeeben, Martin, and Oncina has been shown to be comparable to the results

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EI(NOx)
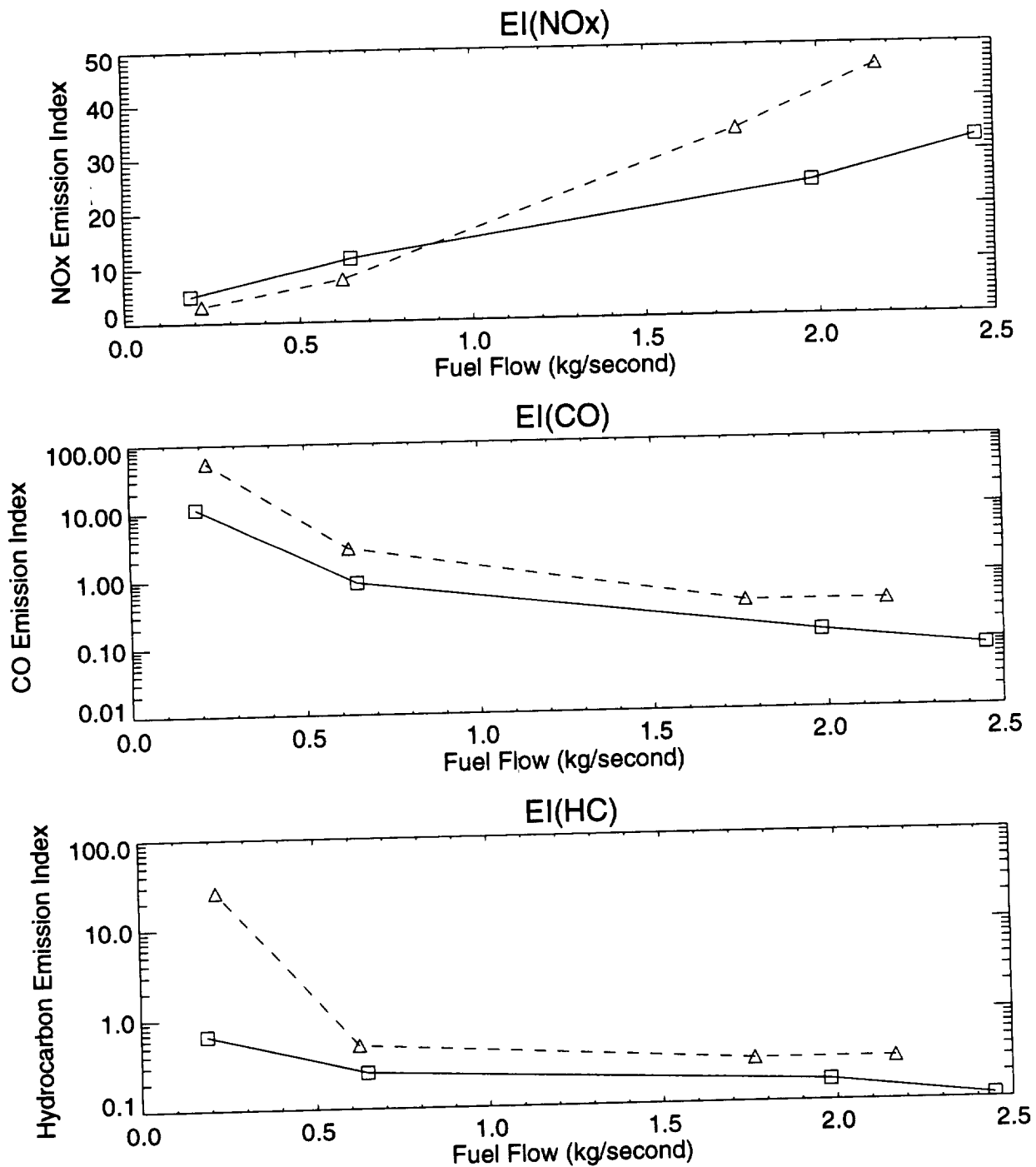

EI(CO)

EI(HC)

Figure 2-1. Comparison of emission indices for NO_x, CO and hydrocarbons for the PW4056 (solid line) and JT9D-7F (dashed line). These values are for standard day conditions at sea level. EIs are given in units of grams/kilogram fuel burned.

obtained using the standard P_3/T_3 method mentioned above with a complete thermodynamic cycle analysis. Since all methods for calculating EI_{NO_x}, whether by P_3/T_3 or fuel flow correlation, depend on a reliable description of the combustor conditions, accurate data on the aircraft performance and fuel flow rates are critical.

In Table 2-2, average EIs for a number of aircraft in service are shown for two altitude bands: 0 to 9 km (corresponding to takeoff, climb, descent, landing, and taxi operations) and 9 to 13 km (corresponding to cruise and, in some cases, a portion of the initial climb to start of cruise). These EIs were obtained by calculating individual emission inventories for each aircraft type as it was used in April 1992 and then analyzing the fuel burned and emissions in the two altitude bands. Calculations were done for the different engines used by that aircraft type and then totaled. For each aircraft type, the daily fuel use and that aircraft's fraction of the total by all scheduled aircraft also are shown. More detailed results are shown in Baughcum *et al.* [1996].

Table 2-2 illustrates that no single aircraft dominates the emission inventory and that a relatively large number of aircraft must be considered in the calculations. In general, as the combustor efficiencies have improved, EIs for CO and hydrocarbons have decreased while NO_x EIs have increased. This table highlights the range of EIs which may occur. In addition, improvements in aircraft/engine performance have reduced the fuel use per passenger mile as new generations of aircraft have been developed. Thus, while some aircraft types have similar EIs, their fuel use per passenger mile may vary.

EMISSIONS INVENTORY CALCULATION PROCESS

In order to calculate an inventory of aircraft emissions, data on flight frequencies, aircraft performance, and engine emissions must be combined. The process used by Boeing for scheduled commercial air traffic is described below. A similar process is used for the calculation of other components. Flights within the former USSR and People's Republic of China and charter flights are not listed in published databases, and their schedules must be obtained or estimated from other sources. For the military aircraft, the altitude profiles may be determined by the operational procedures or typical mission for that aircraft and flight frequencies can only be estimated.

(1) A schedule of aircraft frequencies between cities (i.e., city pair) for each aircraft type is extracted from flight schedules (e.g., the Official Airline Guide (OAG)). Specifying the exact aircraft/engine combination for a given flight involves matching airline flight number with the aircraft models and engines used by that airline. It also requires eliminating duplicate flight numbers for the same airline, code sharing of flights between two airlines (shown as two flight numbers but with only one flight), and data ambiguity.

(2) The aircraft/engine combinations used by the airlines are matched to a list of aircraft for which detailed performance data is available. This performance database relates fuel burn and optimum flight altitude to weight of the aircraft. Typically, the available performance dataset is a much smaller subset of the total number of aircraft/engine combinations in use by the airline. For the latest NASA analyses, we have matched approximately 230 aircraft/engine combinations in use by the airlines to a performance dataset consisting of 78 aircraft/engine combinations.

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Table 2-2. Emission indices for commercial aircraft types (based on April 1992 scheduled air traffic).

Airplane Type	Fuel (1000 kg/day)	% of Global Fuel Burned by Scheduled Traffic	0- to 9-km Altitude Band			9- to 13-km Altitude Band		
			EI (NO$_x$)	EI (CO)	EI (HC)	EI (NO$_x$)	EI (CO)	EI (HC)
Boeing 747-200	26,359	10.4%	22.8	22.8	12.8	14.2	1.4	0.8
Boeing 747-100	22,519	8.9%	23.4	22.2	12.1	13.9	0.4	0.6
Boeing 727-200	21,478	8.5%	11.6	5.0	0.8	8.7	2.4	0.5
DC-10	19,140	7.5%	21.0	17.6	6.5	13.2	2.0	1.3
MD-80	16,122	6.4%	14.3	5.3	1.5	10.6	3.3	1.2
Boeing 737-200	15,563	6.1%	10.2	6.5	1.4	7.7	2.9	0.6
Boeing 747-400	14,779	5.8%	25.8	8.9	1.6	13.9	1.0	0.4
Boeing 767-200	10,084	4.0%	19.6	6.1	1.3	12.2	2.6	0.6
Boeing 737-300	9,827	3.9%	12.2	15.6	1.3	9.6	2.9	0.2
Airbus A300	9,745	3.8%	20.6	18.9	7.0	14.4	1.2	0.9
DC-9	9,035	3.6%	9.5	9.6	2.7	8.1	2.3	0.5
Lockheed 1011	8,843	3.5%	20.1	19.2	13.5	15.0	1.9	0.7
Boeing 757-200	8,052	3.2%	17.3	10.4	0.9	12.6	2.0	0.2
Boeing 747-300	5,772	2.3%	24.4	15.5	9.6	14.5	1.9	0.5
Tupolev 154	5,610	2.2%	11.8	4.7	0.7	8.7	2.2	0.5
Airbus A310	4,682	1.8%	19.6	6.7	1.4	13.6	2.0	0.5
Boeing 767-300	4,536	1.8%	18.0	11.7	3.0	13.4	2.3	0.6
DC-8	4,397	1.7%	7.5	43.5	37.2	5.6	7.0	2.0
Airbus A320	3,653	1.4%	16.1	6.8	0.5	12.1	2.0	0.4
Boeing 727-100	3,107	1.2%	10.9	7.4	2.2	7.7	3.7	1.1
Small Turboprops	2,975	1.2%	8.1	4.0	0.2			
MD-11	2,841	1.1%	19.6	9.7	1.5	12.4	1.6	0.2
Boeing 747-SP	2,573	1.0%	23.2	30.6	19.9	14.4	1.1	0.8
Large Turboprops	2,126	0.8%	13.0	4.3	0.0			
Boeing 707	2,101	0.8%	15.1	39.1	44.7	5.9	8.0	7.9
Ilyushin 62	1,974	0.8%	14.6	34.2	39.5	5.9	5.9	6.0
Medium Turboprops	1,944	0.8%	11.8	5.1	0.6			
Boeing 737-400	1,787	0.7%	12.2	15.0	1.1	9.6	3.5	0.2
Fokker 28	1,680	0.7%	10.5	6.0	0.5	8.5	1.5	0.4
BAE-146	1,548	0.6%	8.8	8.1	0.8	7.7	0.2	0.0
Airbus A300-600	1,539	0.6%	18.9	10.9	2.0	13.2	2.0	0.4
Boeing 737-500	1,497	0.6%	11.4	12.9	0.8	9.4	3.8	0.2
Ilyushin 86	1,264	0.5%	15.1	38.8	44.7	5.8	8.1	8.0
Fokker 100	1,003	0.4%	9.5	25.9	2.5	6.4	11.5	1.6
Tupolev 134	846	0.3%	9.4	9.3	2.9	8.0	2.1	0.5
Boeing 747-SR	673	0.3%	18.6	19.3	11.1	14.0	2.7	2.7
BAC 111	544	0.2%	11.4	13.4	2.3	9.3	2.7	0.6
YAK 42	460	0.2%	10.8	7.4	2.2	7.6	3.8	1.1
Concorde	404	0.2%	10.4	27.9	5.4	10.0	26.0	1.8
Ilyushin 72	248	0.1%	15.1	38.7	44.5	5.8	8.0	7.9

(3) For each engine type considered in the dataset, a file of EIs as a function of fuel flow is obtained from the ICAO Engine Exhaust Emissions Databank [ICAO, 1995].

(4) For each flight, the takeoff gross weight of the aircraft is calculated from the flight distance (assuming great circle routing), including fuel reserves and an assumed 70% passenger load factor. The altitude as a function of distance is determined from the gross aircraft weight for the mission. The fuel burn rate is calculated from the performance data as a function of distance. From the fuel burn rate, the EIs are calculated using the emission fuel flow methodology mentioned above, with corrections for ambient corrections. The mission profile is then developed on a three-dimensional grid (e.g., 1° latitude x 1° longitude x 1 km altitude resolution).

(5) Step (4) is repeated for all flights.

For projections to future years, passenger demand is projected for different geographical regions to create future departure frequencies for different sizes of aircraft. Future aircraft performance and emission characteristics are projected based on modern aircraft characteristics and projected improvements/changes [Wuebbles et al., 1993; Baughcum et al., 1994].

INVENTORY RESULTS TO DATE

Aircraft emission inventories produced as part of the NASA AESA program for 1990 and projected to year 2015 have been reported previously [Wuebbles et al., 1993; Baughcum et al., 1994; Landau et al., 1994]. As shown in Figure 2-2, peak emissions occur in two altitude bands: 0 to 1 km during takeoff and 8 to 13 km during cruise. The majority of emissions occur in the Northern hemisphere with most emissions at mid-latitudes. By contrast, many regions of the Southern hemisphere are expected to be relatively uncontaminated by aircraft emissions.

The global emission totals are summarized in Table 2-3. The tables assume that May 1990 is typical of the annual average, consistent with passenger flow statistics. For 1990, the majority (68%) of aircraft fuel use is calculated to arise from scheduled commercial airline and cargo jet operations. Military (19%), turboprop aircraft (1%), charter (5%), and non-OAG scheduled air traffic within the former Soviet Union and China (6%) account for the remaining calculated fuel use.

Fuel use by world civil aviation for 1990 has been reported to be 1.33×10^{11} kg/year for commercial airlines and 0.035×10^{11} kg/year for general aviation [Balashov and Smith, 1992]. These numbers are 19% higher than that calculated above for scheduled traffic, charter, turboprop, and former Soviet Union air traffic.

For comparison, refinery production of distillate labeled as jet fuel at the refinery and provided by different countries was reported as 1.76×10^{11} kg/year for 1990 [Department of Energy, 1991], approximately 22% higher than that calculated in the NASA study. This is not a "perfect" dataset for comparison, however, because it does not necessarily represent jet fuel delivered to airports. Jet fuel is a fungible product and can be reclassified and sold as kerosene or mixed with fuel oils

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Total aircraft emissions 1990

Altitude (km) vs Latitude

log NOx (lb/day)
2.00   2.75   3.50   4.25   5.00

Latitude vs Longitude

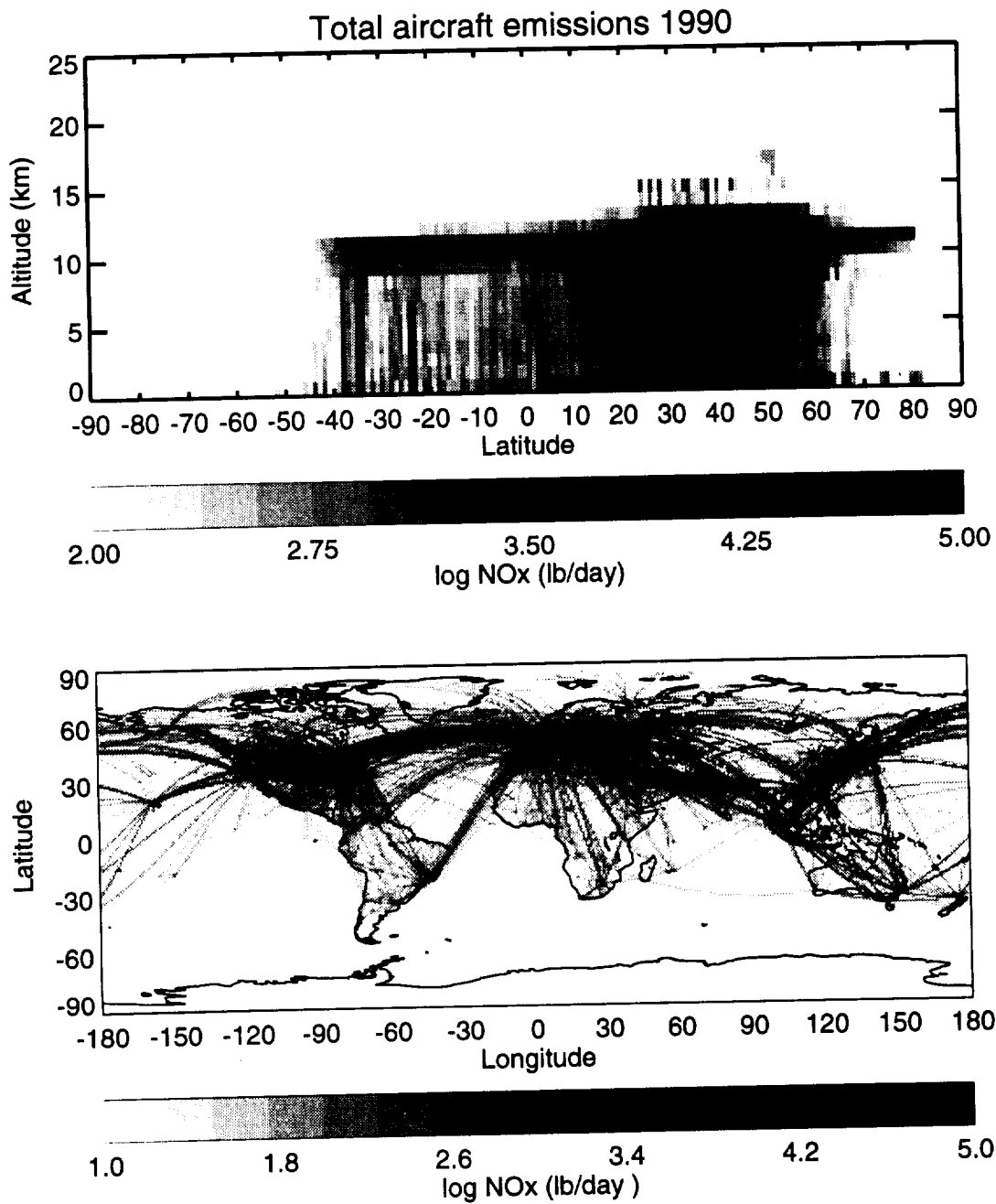log NOx (lb/day)
1.0   1.8   2.6   3.4   4.2   5.0

Figure 2-2. NOx emissions for all 1990 aircraft traffic as a function of altitude and latitude (summed over longitude) (top panel) and as a function of latitude and longitude (summed over altitude) (bottom panel).

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Table 2-3. Summary of fuel burn and emissions from each of the component databases and scenarios[*].

File	Fuel (kg/yr)	NO$_x$ (kg/yr)	HC (kg/yr)	CO (kg/yr)
1990				
Scheduled Airline and Cargo	9.08E+10	1.14E+09	1.37E+08	5.17E+08
Scheduled Turboprop	1.99E+09	2.05E+07	1.11E+06	9.77E+06
Charter	6.65E+09	5.99E+07	4.08E+06	3.42E+07
Military	2.60E+10	1.94E+08	1.89E+08	4.86E+08
Former Soviet Union	8.28E+09	4.92E+07	2.17E+07	8.20E+07
Total (1990)	1.34E+11	1.46E+09	3.52E+08	1.13E+09
2015				
Scheduled Cargo	5.64E+09	4.91E+07	3.56E+06	2.77E+07
Scheduled Airline (no high-speed civil transport (HSCT) fleet)	2.45E+11	2.24E+09	9.20E+07	1.09E+09
Scheduled Turboprop	4.14E+09	4.42E+07	7.27E+06	2.41E+07
Charter	1.35E+10	1.22E+08	8.91E+06	7.23E+07
Military	2.06E+10	1.47E+08	1.85E+08	4.05E+08
Former Soviet Union	1.58E+10	9.38E+07	4.13E+07	1.56E+08
YR 2015 Total (no HSCT fleet)	3.04E+11	2.70E+09	3.38E+08	1.77E+09

[*] $1.0E + 08 = 1 \times 10^8$

and diesel fuels depending on market requirements (e.g., when a low freezing point fuel is needed in the winter). Also, some other distillate fuels from the refinery may satisfy jet fuel requirements and ultimately be purchased and used as jet fuel. Thus, while the refinery reports serve as a useful comparison, they cannot be used as an absolute standard. Also, the invasion of Kuwait and the buildup for the Persian Gulf war probably makes 1990 an atypical year for military fuel use.

Two related global inventories of aircraft emissions have been developed recently. McInnes and Walker [1992] accounted for 51% of the total jet fuel use for 1989 and then scaled their dataset to match the values reported in the International Energy Annual. The European Abatement of Nuisance Caused by Air Traffic (ANCAT) study is still being revised and preliminary results are now available [Schumann, 1995].

SEASONALITY

Air traffic varies with the seasons with peak travel occurring during the summer. To account for this quantitatively, inventories of aircraft emissions have been developed for each month of 1992 for scheduled air traffic [Baughcum et al., 1996] and for military, charter, and non-scheduled Russian air traffic [Metwally, 1995].

Figure 2-3 illustrates the seasonal cycle in NO_x emissions in the 9- to 13-km altitude band for scheduled air traffic during 1992 [Baughcum et al., 1996]. The top panel shows the daily emission levels for four regions: North America, Europe, the North Atlantic, and the North Pacific. (Author's note: For this analysis, the regions are defined as simple rectangular boxes with the following definitions: North America - 25°N to 70°N latitude, 125°W to 70°W longitude; Europe - 37°N to 70°N latitude, 10°W to 25°E longitude; North Atlantic - 30°N to 70°N latitude, 70°W to 10°W longitude; and North Pacific - 30°N to 65°N latitude, 120°E to 125°W longitude.) The percent deviation from the annual mean is shown in the bottom panel. The North Atlantic shows the largest seasonal variation with modulations of approximately ±18%. The other regions also show peak emissions during the summer and minimums during the winter.

UNCERTAINTIES AND ERROR ANALYSIS

A number of simplifying approximations are made in the calculation of these global inventories:

- Aircraft are assumed to fly according to design performance with fuel consumption and flight altitude determined by aircraft gross weight.

- Aircraft fly great circle routes between cities.

- The effects of winds is averaged by having flights in both directions (zero prevailing winds).

- Standard day temperatures are assumed for all flights.

- Aircraft fly with the correct amount of fuel for the mission plus safety reserves. No fuel tankering occurs. Tankering is the practice of carrying enough fuel so that several flights are made without refueling, in order to save time.

- Airports are treated as point sources with flights taking off and landing in the direction of their destination. No special procedures are considered for different airports; all are treated alike.

- Congestion, both in the ground and in the air, is not considered. Weather effects are not included.

- Fuel use by auxiliary power units is not considered.

- All aircraft are assumed to fly with the same 70% load factor and no cargo other than passenger luggage.
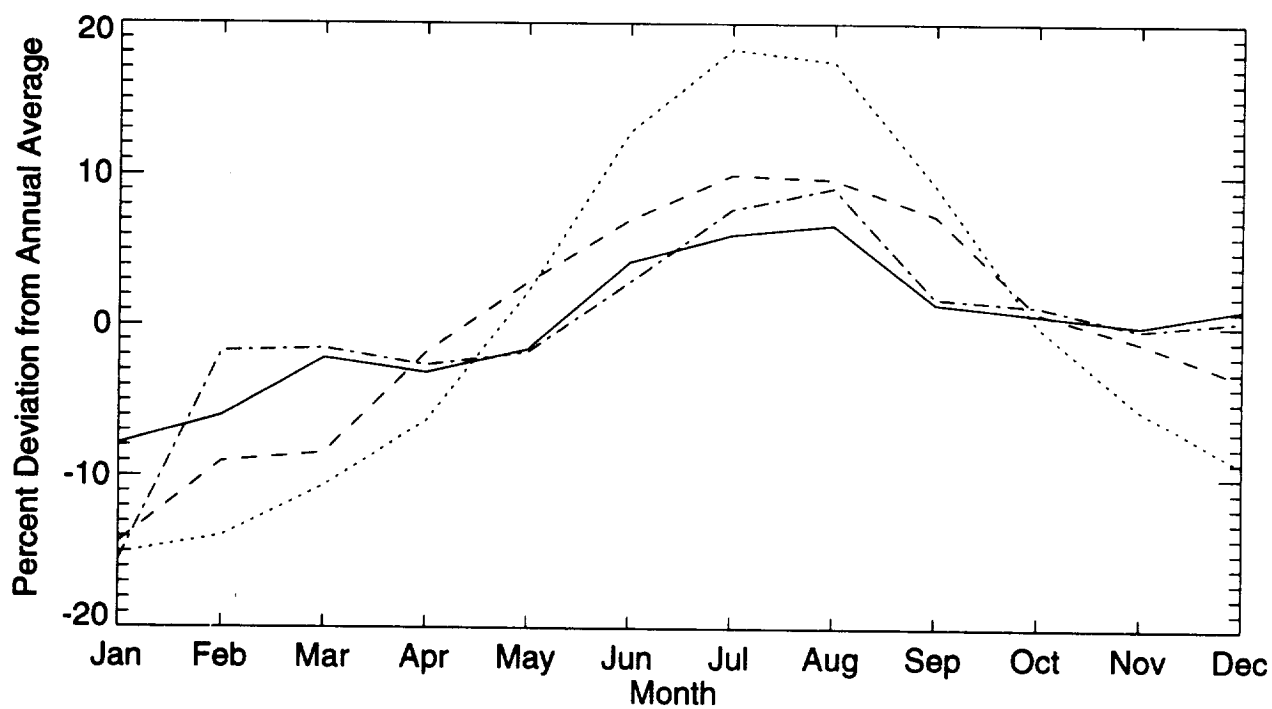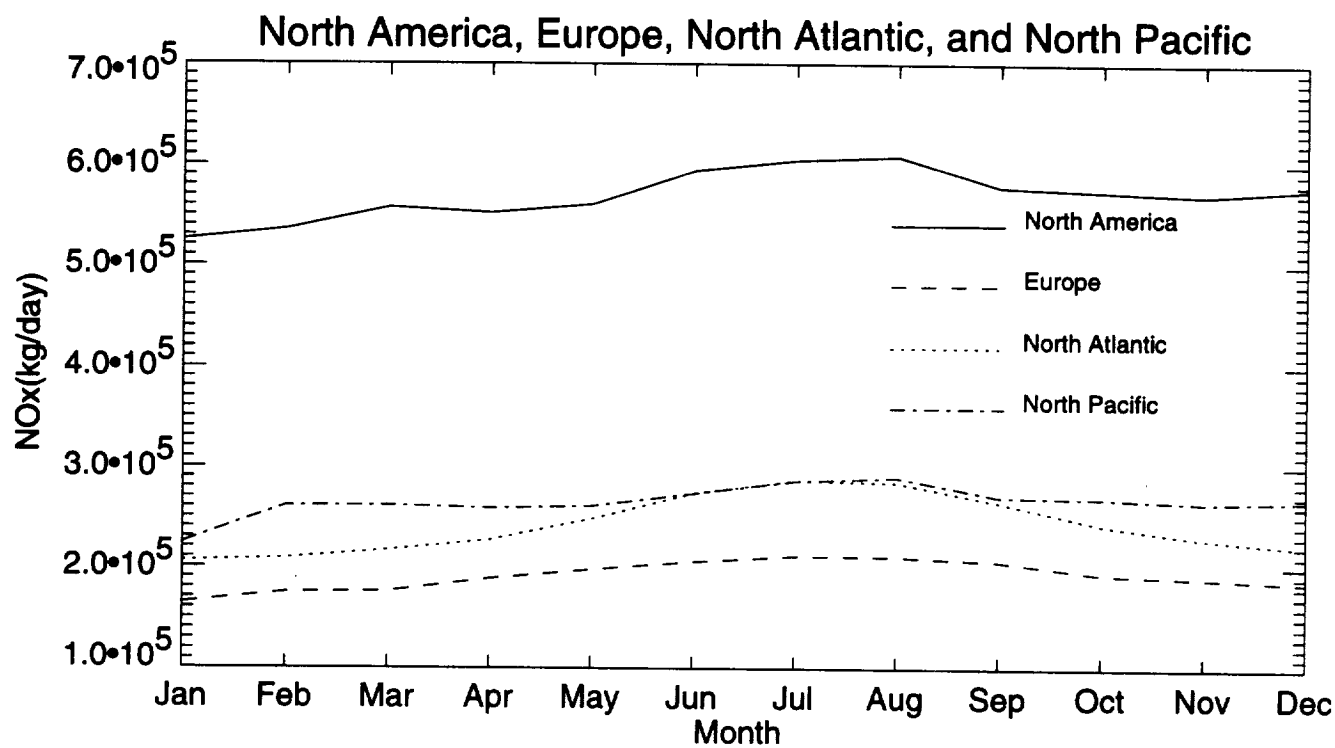
Figure 2-3. NO_x emissions in the 8-13 km altitude band for scheduled air traffic in 1992 for North America (solid line), Europe (dashed line), the North Atlantic (dotted line), and the North Pacific (dash-dot line).

Since some of these simplifying assumptions may lead to systematic errors, a series of parametric studies are underway to evaluate their importance [Baughcum et al., 1996]. Some preliminary results are presented here.

Meteorological effects are evaluated using a database of monthly means and standard deviations of winds and temperatures derived from daily National Meteorological Center (NMC) analyses between July 1976 and June 1985. This database is incorporated into the Boeing WINDTEMP program for use by both airline route planners and design engineers to calculate winds and temperatures en route between two selected cities. The code is integrated with Boeing's performance analyses so that the effect of winds and temperatures on fuel consumption on a given route can be calculated explicitly for different months of the year and for different reliabilities.

Using this meteorological data and flying great circle routes between the cities, the effects of winds and temperature on fuel use in selected regions was evaluated (Los Angeles - Tokyo, New York -London, New York - Rio de Janeiro). The effect of non-standard temperatures was found to be small, 0.3 to 0.5% on east-west flights and 0.7% on the north-south flight. To first order, prevailing winds in route would be expected to cancel out since flights are going in both directions; but flights into the wind take longer, must carry more fuel, and thus burn fuel at a higher rate than for flights with the wind. Calculations indicate that wind effects are about 0.4% for the north-south route (average head wind = 9 knots) and 1.1 to 1.8% for the east-west routes (average headwinds = 42 to 50 knots). Considering both wind and temperature effects together, the effect is slightly less than additive. Thus, the assumptions of standard day conditions and zero prevailing winds lead to an under prediction of fuel use of 1 to 2%. In actual airline operation, where air traffic control permits, aircraft will be routed to minimize fuel usage taking advantage of the winds.

Heavier aircraft burn fuel at a higher rate than do lighter weight aircraft. Thus, the actual fuel usage for a flight is sensitive to the distance flown, the passenger load, the cargo load, and any extra fuel carried. This increased fuel burn rate for a given mission will result in higher NO_x EIs as well. As an example, fuel use per nautical mile at cruise conditions for a 747 increases from approximately 36.5 pounds/nmi for a 2000-nm mission to 44 pounds/nmi for a 7000-nm mission.

To evaluate the effects of fuel tankering, a Boeing 737 was modeled on flights between Los Angeles and San Francisco. For this 293 nautical mile flight, the aircraft can carry enough fuel for four flights. Assuming the aircraft fueled for all 4 flights, the average increase in fuel use per flight was calculated to be 4%. This is an extreme case since most aircraft fly much longer distances and tankering is less important.

In a similar study related to aircraft weight effects, a Boeing 747 was modeled on a flight from Los Angeles to Tokyo. Increasing the average passenger weight allowance (passenger + baggage = 200 pounds) to 230 pounds increased mission fuel use by 1.1%. Similarly, increasing the load factor from 70 to 75% increased fuel use by 0.8%. Flying the aircraft at maximum cargo weight increased fuel use by 13.2%. With a more typical cargo density (10 pounds/ft^3) and the cargo hold completely full, fuel use for the mission would increase by 7.7%. Since most aircraft do not have the cargo capacity of a 747, work is still underway to evaluate how this result should be extended to the global inventory.

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WORK IN PROGRESS AND FUTURE WORK

The monthly emission inventories for 1992 are now being completed and will be available to the modeling community early in 1996. Work is underway to develop aircraft emission inventories for selected months of 1976 and 1984. This historical dataset will then be used to evaluate historical trends in aircraft emissions and can be used for trend analyses in modeling calculations. The inventories will include scheduled commercial passenger and cargo flights, military, charter, and internal flights within the former USSR.

In addition, parametric studies continue to evaluate the errors and uncertainties in the magnitude and geographical distributions of the emissions. This work has initially focused on evaluating simplifying assumptions on fuel use but is being extended to evaluate their effects on NO_x EIs as well. These parametrics have focused on placing upper bounds on some of the simplifying assumptions. The next step would be to more realistically evaluate how these effects relate to the overall accuracy of the emission inventories.

Comparisons of the NASA emission inventories and the preliminary datasets of the European ANCAT study have shown differences in both fuel use and NO_x emissions. Work is underway to understand the sources of those differences. Since NO_x EIs depend on the combustor temperature and the fuel flow rate, errors in the calculation of the fuel use will be compounded by subsequent errors in EI_{NO_x}.

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Chapter 3

Emissions Characterization

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INTRODUCTION

The potential environmental perturbations from the gases and particulate exhaust emissions of high-speed civil transports (HSCTs) and the subsonic aircraft fleet depend on flight scenarios, combustor type and stoichiometry, engine design, operating parameters, and deposition altitude. Assessing the possible perturbations which may result over the next 25 years requires developing a firm understanding of both the present operating fleet characteristics and how these characteristics might change as propulsion designs continue to evolve toward higher efficiency, low-emission systems. This section deals with engine emittant measurements utilizing several techniques for engine types currently in the fleet, new engines/combustors, and future engine combustors.

In the case of HSCTs, no aircraft and/or prototype engines are currently operating. Since 1989, the NASA High-Speed Research Program (HSRP) has been investigating, along with General Electric Aircraft Engines (GEAE) and Pratt & Whitney (P&W), new, low-emission, gas turbine combustor concepts based on lean, prevaporized, premixed (LPP) and rich-quench-lean (RQL) designs that would likely be the prototypes for future propulsion systems. The Atmospheric Effects of Stratospheric Aircraft (AESA) component of HSRP has been assessing the environmental impacts of future high-speed aircraft fleets based upon current combustors and advanced laboratory combustors of assumed emission indices (EIs) at operating conditions for the fully developed systems. The AESA program has concentrated specifically on perturbations in the 18- to 22-km region of the stratosphere and on aircraft emission perturbations of ozone chemistry. Considerable advances have been made on understanding of issues raised in earlier studies, indicating perhaps a somewhat reduced, but continuing, primary importance of nitrogen oxides (NO_x) emissions to this issue, and pointing to a previously unrecognized (and significant) role of heterogeneous chemistry. Recent multi-dimensional modeling also indicates a significant importance of vertical mixing of upper tropospheric materials into the lower stratosphere, as well as ground level materials into the troposphere.

More recently, questions have arisen as to the impact of present and future subsonic aircraft on the environment. Whereas a large and diverse subsonic fleet has been operating for some time, the impact of its operation on the present state of the upper troposphere is neither obvious nor easily separable from other perturbations. At present, there is little on which to base estimates of what levels of impact might occur over the next 25 years of subsonic fleet evolution. Indeed, economic and environmental issues alike will stimulate considerable efforts to design new, higher performance/efficiency, lower emission, gas turbine propulsion concepts for subsonic aircraft. As yet unspecified low-emission, high compressor ratio combustion concepts for subsonic aircraft are the subject of new research under the NASA Advanced Subsonic Technology Program (ASTP). As part of this effort, the Subsonic Assessment (SASS) Program, coordinated with AESA through the Atmospheric Effects of Aviation Project (AEAP), has been initiated. The SASS effort not only extends the region of interest to the lower stratosphere/upper troposphere (8 to 12 km, where most subsonic transports operate), but also adds consideration of the radiative (climatic) impact of aircraft emissions, both from ozone layer/greenhouse gas effects and aerosol/cloud scattering. The SASS issues clearly differ from those of AESA at zeroth order, since a substantial subsonic fleet is already operating and climatic impacts of aircraft have not been considered previously. Evidence of subsonic aircraft might be apparent if appropriate interpretation of existing *in situ* and remote sensing data were to be developed. Similar to the approach taken historically within AESA,

atmospheric modeling efforts can be mounted to shed light on present subsonic fleet effects and extrapolate those into the future. Major propulsion differences between supersonic and subsonic propulsion systems are:

- Future combustors for supersonic aircraft will operate in the 10- to 14-atmosphere pressure range.

- Present subsonic combustors operate in the 30-atmosphere range with pressure increases up to 60+ atmospheres likely by the year 2000.

- Higher pressures result in more soot, carbon formation, and faster reactions with different exhaust constituent mix.

- Unlike the HSRP, the right engines are available now for subsonic tests of advanced combustor concepts except for those being developed for year 2000+ introduction.

- Ultra-low-NO_x advanced subsonic combustor concepts may well be quite different than HSRP concepts.

Since none of the future, advanced, low-emission engine designs (supersonic or subsonic) are expected to achieve full-scale configuration until after the turn of the century, characterization of the emissions in flame tube, single- and multi-sector, and full-scale combustor tests will play a principal role in their design. Yet, it is the full scale parameters which will eventually impact the environment. While total engine emissions from aircraft are in large measure influenced by the combustor design and operating parameters themselves, distributions of molecular constituents including nonmethane unburned hydrocarbons (NMUHC), carbon monoxide (CO), nitric oxide (NO), nitrogen dioxide (NO_2), and carbon-containing particulates present at the exit of the combustor continue to chemically interact through radical-controlled, nonequilibrium kinetics, in the turbine and nozzle hot sections to yield a final constituency to the exhaust at the engine exit plane. Such transformations are known to occur in current generation engines and are not understood in terms of predictive modeling. The impact of such chemistry on exit-plane composition is likely to become even more significant when compressor ratio and turbine inlet temperatures are increased. Understanding these effects ior full-scale engine configurations and operating parameters will be necessary to assess the environmental impact of particular designs, especially if plume/wake dispersion and mixing processes increase in importance.

Finally, in both HSCT and subsonic flights, additional processing of engine exhaust-plane constituents occurs during the wake/plume dispersion and mixing behind the aircraft to yield those species which will, over the longer term, participate in atmospheric chemistry and potentially cause changes in ozone concentrations and climatic parameters. The significance of these processes has not yet been fully assessed for stratospheric deposition [Miake-Lye *et al.*, 1993a, b; Kolb *et al.*, 1993], but are speculated to be different in the upper troposphere/lower stratosphere (UT/LS) scenarios. Plume dispersion and mixing times are of different scales because of aircraft aerodynamic and atmospheric mixing times, backgrounds for water, ozone, NO_x (NO, NO_2), and reactive halogens change with altitude. Potentially larger contributions from non-aircraft pollutant sources of NO_x, sulfur oxides (SO_x), aerosols, CO, hydrocarbons (HCs), carbon dioxide (CO_2),

and carbon-containing particulates may exist at these lower altitudes. Emissions chemistry embodied within plume dispersion and mixing models will be needed to define most appropriate tracers for experimental dispersion measurements, to define local chemical transformations, and to develop appropriately parameterized sub-model elements for global modeling. Engine exhaust plane emissions are therefore an important initial condition upon which the validity of any such predictions will depend.

ENGINE EXHAUST TRACE CHEMISTRY (EETC) COMMITTEE

In 1992, the Engine Exhaust Trace Chemistry (EETC) Committee was organized to provide guidance and recommendations to the HSRP/AESA in developing a future engine emissions measurement and assessment program. The committee is composed of representatives from the range of disciplines that will contribute to this measurement effort. Combustor emission researchers and developers met to formulate a trace chemistry program. Members include those with backgrounds in combustion research, atmospheric measurement, and particulate measurement, and those with relevant aerodynamic or engine expertise. A list of committee members follows

F. Dryer, Chair	Princeton University (Chair), Princeton, NJ
J. Facey	NASA Headquarters, Washington, DC
D. Fahey	NOAA Aeronomy Laboratory, Boulder, CO
A. Hansen	Lawrence Berkeley Laboratory, Berkeley, CA
D. Hagen	University of Missouri, Rolla, MO
P. Heberling	General Electric Aircraft Engines, Cincinnati, OH
R. Howard	Arnold Engineering Development Center, Arnold AFB, TN
C. Jacimowski	NASA Langley Research Center, Hampton, VA
S. Langhoff	NASA Ames Research Center, Moffett Field, CA
H. Lilenfeld	McDonnell Douglas, Saint Louis, MO
R. Lohmann	Pratt & Whitney, East Hartford, CT
N. Marchionna	Stirling Thermal Motors, Inc., Ann Arbor, MI
R. Miake-Lye	Aerodyne Research, Inc., Billerica, MA
R. Niedzwiecki	NASA Lewis Research Center, Cleveland, OH
R. Oliver	Institute for Defense Analyses, Alexandria, VA
R. Pueschel	NASA Ames Research Center, Moffett Field, CA
C. C. Wey	Army Research Laboratory/NASA LeRC, Cleveland, OH
P. Whitefield	University of Missouri, Rolla, MO
K. Wolfe, Executive Secretary	Computer Sciences Corporation, Lanham-Seabrook, MD
J. Wormhoudt	Aerodyne Research, Inc., Billerica, MA

The initial premise for developing the EETC was to (1) identify and rank which species are important to know in order to define what engines are depositing into the atmosphere, (2) determine priorities and recommend venues for measuring these quantities, and (3) determine how best to make the measurements and the accuracy of the methods chosen. Such an effort is needed to provide evidence that the actual emissions characteristics of HSCT aircraft are indeed consistent with those characteristics used in the stratospheric modeling segment of the program. Two major challenges are (1) as advances are made in understanding atmospheric effects, the specific

emissions that need to be quantified may change; and (2) HSCT engine development will not reach full systems testing, under either ground or flight conditions, until some time after 2000. Thus, the EETC must deduce exhaust emissions levels for aircraft engines well before they have been prototyped and tested. This will be accomplished by obtaining data from advanced combustor flame tubes; combustor sector, full-annular combustors; existing engines; and by conducting fundamental analytical studies and laboratory experiments.

The initial efforts of the EETC have therefore concentrated on prioritizing engine trace constituent measurement requirements for assessing HSCT impacts, based upon (in decreasing priority): (1) direct impact on ozone chemistry in the stratosphere, (2) those exhaust components which might affect wake/plume chemical and condensation phenomena, and (3) those which might serve as design optimization indicators in engine development.

In October 1993, a NASA Research Announcement (NRA) was released calling for additional proposed research to address five specific areas in which SASS has initially identified needs. Two of those areas, (4) Near-Field Interactions and Plume Mixing/Dispersion and (5) Engine Exhaust Characterization, are closely related to prior considerations of the EETC. As a result, the EETC was requested to provide some guidance on what modifications/new issues would be important, beyond those already considered from the point of view of AESA.

A Committee meeting to address these matters was held on 2 November 1993, in Billerica, MA. The objective was to define near-term and long-term (i.e., an eight-year program) research priorities in the EETC area. The following recommendations were made:

- Experimentally determine cruise emittants for current engine/combustors, advanced engines/combustors, and ultra-low emission combustors with extractive sampling techniques and independent nonintrusive techniques at combustor exit planes and engine nozzle exit planes.

- Develop an analytical and experimental technology base for relating combustor emittants with engine exhaust nozzle exit-plane emittants. This technology base, focused on the hot section and engine nozzle interactions, should include development of appropriate interaction chemistry, reactive flow models, and the necessary engine data for model validation.

- Develop measurement/venue scenarios for obtaining cruise operation/altitude engine emission measurement species as prioritized in the AESA studies.

- Evolve a nonintrusive sampling technique for obtaining emission constituents under the high-pressure conditions encountered in combustor test facilities. Otherwise utilize the sampling techniques evolved under AESA. Emphasis should be directed towards assuring that extractive measurements accurately characterize in situ emittants.

- Assist in obtaining exhaust emittants under flight conditions. This activity should be conducted by other program elements in close coordination with and assistance from the EETC.

On the basis of these recommendations, an emissions characterization program was assembled and discussed at an EETC meeting in the spring of 1994. Several new research projects were initiated and an engine test program was identified.

MEASUREMENT TECHNIQUES AND ANALYTICAL METHODS

Existing and promising state-of-the-art measurement techniques to obtain both combustor and engine exit-plane measurements, as well as measurement venues, were also reviewed and prioritized. Results of these studies were published in NASA Reference Publication 1313 [Stolarski and Wesoky, 1993].

Various extractive sampling/quenching techniques and analytical instruments are conventionally employed today in engine development and qualification tests to obtain molecular constituents such as nonmethane hydrocarbons (NMHC), NO, NO_2, and CO, while "particulates" are typically evaluated in terms of extractive sampling and smoke number determinations. In the course of the EETC work, a consensus developed that the accuracy of extractive sampling methodologies should be reconfirmed for HSCT operating conditions, that redundancy of measurements should be considered, especially if both extractive and *in situ* methods could be simultaneously applied, and that smoke number methods needed to be augmented with more direct, quantitative methods which would yield particulate mass and number density results.

As a result of an AESA NRA competition in 1992, two additional research areas impacting diagnostics were added to those which had previously been part of the AESA effort. The first effort is to implement and demonstrate tunable diode laser (TDL) absorption technology for the measurement of combustor and exhaust-plane gaseous emission species. The second is to develop and apply the mobile aerosol sampling system (MASS) differential mobility analysis approach to determine particulate mass, number density, size distribution, and hydration properties [see also Whitefield *et al.*, 1993; Hagen *et al.*, 1993]. As a part of the SASS effort, three more research projects were implemented to improve understanding of the emissions interactions in the hot- and nozzle-engine sections. One is to develop and validate the chemical kinetic mechanisms of combustor exhaust components over the pressure and temperature ranges of interest. Another is to determine the influence of the three-dimensional (3-D), unsteady turbine and nozzle flows on the evolution of primary pollutants, trace species, and aerosols through calculation of full pollutant chemistry in the complex flowfield of the turbine and nozzle. The third project is to develop *in situ* optical methods for the measurements of NO and hydroxyl radical (OH) using line-of-sight methods.

Each of these instruments/computational modeling methods will be used to provide measurements in fundamental combustion, combustor development, and engine test-stand venues. Additional data being obtained at the NASA Lewis Research Center, P&W, and GEAE, including exhaust-gas probe sampling, laser induced fluorescence (LIF), gas chromatograph/mass spectrometer (GC/MS) and focused schlieren, will supply additional baseline data and be used for comparative purposes.

CURRENT STATUS

A summary of the research activities underway is contained below.

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Aerodyne Research, Inc. (ARI) started the development of a TDL differential infrared absorption system to provide nonintrusive and extractive sampling measurement in 1993. This effort provides a multi-species system that is able to be used in both *in situ*, single or multipass, and extractive sampling, low-pressure multipass cell configurations. This system can provide redundant measurements on NO_x, as well as a full characterization of all reactive nitrogen (NO_y) emissions species, with advanced versions providing measurements of sulfur dioxide (SO_2), sulfur trioxide (SO_3), CO_2, CO, and OH. TDL measurements of NO and NO_2 were obtained in the NASA Lewis Research Center (LeRC) LPP flame tube facility in 1994. The conclusion of this test was that general agreement with LeRC gas sampling probe data (NO and NO_2 by chemiluminescent analyzers) and evidence for NO/NO_2 interconversion in the sampling line were observed. Measurements of NO, NO_2, and CO_2 were obtained for the Arnold Engineering Development Center (AEDC) engine test on 25 October 1995. Data are being analyzed and will be compared with both AEDC gas sampling system data (NO and NO_2 by using chemiluminescent analyzers) and AEDC optical measurements (NO by using UV resonance absorption techniques). Results will be presented in mid-1996.

University of Missouri, Rolla (UMR) started the development of MASS in 1993. This system provides the measurements of the exhaust particulate total mass, total number density, size distribution, and hydration properties. Measurements were made on a United Technologies Research Center RQL rig in August 1994 and resulted in the development of a unique sample pressure reduction facility. The general conclusions of this measurement activity are that log-normal size distributions typical of other jet engine measurements were observed, the particulates possessed little or no soluble mass fraction, and the EI for particulates ranged from 0.2 to 0.9 g/kg with a mean value of 0.5. Measurements were also obtained in the AEDC engine test in October 1995. Analysis of the data is ongoing and will be compared with AEDC smoke number data. Additional analysis will also be performed by this group to characterize the chemical composition and morphology of exhaust particulate. Results will also be presented in mid-1996.

United Technologies Research Center (UTRC) initiated work to develop *in situ* ultraviolet (UV) resonant absorption optical measurement methods for NO and OH in early 1995. This is a three-year effort. The high-pressure flat-flame burner facility has been completed and checked out. Temperature maps along the optical path and detailed probe sampling measurements of NO, NO_2, CO, and CO_2 are in progress. When fully operational, the line-of-sight method will be assessed by obtaining spectroscopic information of molecular absorption at elevated pressures.

Massachusetts Institute of Technology (MIT) started the work of determining the influence of the turbine and nozzle flows on the evolution of combustor species in late 1994. The chemical kinetics, flow interactions, and wake modeling expertise of ARI is incorporated with the gas-turbine fluid mechanics and numerical simulation expertise of MIT. Initial one-dimensional (1-D) investigations were completed. Testing of the fully integrated flow and chemistry code is currently underway with both simple kinetic mechanisms and the full-chemistry kinetic mechanism using a simple geometry. Further testing of the code will use a set of representative engine conditions (temperature, pressure, flow rate, and fuel-air ratio at different stations) provided by LeRC. Results of this research will be used to guide measurements as well as to conduct post-combustor measurement processing.

Princeton University initiated a project to develop and validate the chemical kinetic mechanisms of exhaust species in early 1994. An existing Variable Pressure Flow Reactor (VPFR) and a new High-Pressure Flow-Tube Experiment (HPFE) which is under construction will be used to simulate gas-turbine combustor pressures and temperatures downstream of the combustor exit and to provide an environment in which chemical kinetics, in particular the interactions of CO, model HC, NO_x, and SO_x, can be studied in detail. The database provided by these experiments will be used to develop and validate kinetic mechanisms through numerical modeling. The numerical model thus derived can be utilized to study the interactive emissions chemistry occurring downstream of the combustor and upstream of the engine exit which connects combustor measurement with exit-plane exhaust composition.

The activities described below are being conducted under the emission reduction programs at NASA LeRC.

Particulate data gathered by using a particle counter to obtain number density and size distribution are also being obtained at NASA LeRC. This measurement technique will be applied in February 1996 for LPP and RQL sector combustor tests and in May 1996 for general aviation engine tests. Results will be compared with UMR data.

OH measurements using the planar laser-induced fluorescence (PLIF) technique are being obtained from LPP and lean, direct-injection (LDI) flame tubes and an LPP sector rig at NASA LeRC. OH production, as expected, increases with the fuel-air ratio. Examination of a series of images of single laser pulse showed that the nature of the combustion is not necessarily uniform. This finding was subsequently substantiated by computational fluid dynamics (CFD) calculations. OH measurements will be obtained from an LPP sector rig in February 1996, along with other measurements.

Hydrocarbon speciation measurements using GC/MS were obtained from LPP and LDI flame tubes and an LPP sector rig at NASA LeRC. No compounds higher than C_8 were detected at cruise condition. Some hydrocarbons in the C_4 to C_7 range were identified and the concentrations ranged from several parts per billion by volume (ppbv) to several tens ppbv. There were also unidentified but carbon-grouped hydrocarbons in the C_4 to C_7 range observed at several ppbv to several tens ppbv level. Aldehydes, ethanal (C_2H_4O), propanal (C_3H_6O), butanal (C_4H_8O), and pentanal ($C_5H_{10}O$) were identified without concentration information in almost all the cases. Methane (CH_4) could not be identified under this method. Higher concentrations and larger hydrocarbons were observed at lower fuel-air ratio. GC/MS measurements will be made for the LPP sector rig test in February 1996.

AEDC ENGINE TEST

Emissions tests of an advanced military engine were successfully obtained on 25 October 1995. A variety of sampling techniques, both nonintrusive as well as conventional, were employed. In approximately 10 hours of engine time, several hundreds of data points were obtained. The entire planned test sequence was conducted. Procedures for obtaining engine emission data were demonstrated, which not only satisfy International Civil Aviation Organization (ICAO) requirements but also provide the level of detail required by atmospheric scientists.

The following measurements were obtained:

- A cruciform multi-point rake was used to obtain conventional probe samples of $NO/NO_2/NO_x$ (chemiluminescence), CO, CO_2, molecular oxygen (O_2), and total hydrocarbon (THC) (flame ionization) by AEDC Sverdrup and Air Force personnel. Samples were obtained both at individual and combined locations to determine core/bypass flow regimes.

- Aerosol and soot particulate size distribution, number density, hydration, and reactivity data were similarly obtained by UMR personnel. Smoke number data were also obtained by AEDC and will be compared to UMR data.

- Independent CO_2 measurements were similarly obtained by McDonnell Douglas personnel.

- Nonintrusive TDL measurements of NO/NO_2 and CO_2 were obtained by ARI personnel.

- Nonintrusive UV lamp measurements of NO, OH, and HC speciation were obtained by AEDC Sverdrup personnel.

All the measurements were made under all the following conditions: (1) set point idle, (2) 25 kft at 3 inlet temperatures, (3) 30 kft at 3 inlet temperatures, (4) 40 kft at 3 inlet temperatures, (5) 50 kft at 3 inlet temperatures, and (6) sea-level static including ground idle and 3 power thrust levels. Items (2) through (5) represent a span of simulated cruise flight conditions.

Since the data was obtained for an advanced engine with military classification, special precautions will be employed in the handling and publication of the data. It is EETC's goal to have full disclosure of the relevant data in mid-1996.

FUTURE WORK

Emission data will be acquired in both LPP and RQL sector rigs located at LeRC facilities in February 1996. NO, NO_2, CO, CO_2, THC, and O_2 measurements (using a gas sampling probe system) by LeRC, particulate measurements (using MASS) by UMR, particulate measurements (using particle counter) by LeRC, OH measurements (using PLIF, only available in LPP sector rig) by LeRC, and hydrocarbon speciation measurements (using GC/MS, only available in LPP sector rig) by LeRC will be taken.

A small general aviation type engine will be used to acquire emissions data under simulated altitude conditions at NASA LeRC in 1996. This test presents a unique and cost-effective opportunity to extend the emissions database. Gas-sampling probe rake data of NO, NO_2, CO, CO_2, THC, and O_2 measurements will be obtained, as will particulate measurements using MASS by UMR, particulate measurements using a particle counter by LeRC, and smoke number data. The involvement of ARI measurements is still under discussion.

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Chapter 4

Near Field Interaction - Expanded Workshop Report

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INTRODUCTION

Global model simulations of subsonic aircraft impacts require the input of spatial and temporal distributions of the aircraft exhaust products. Input of aircraft emission inventories into the models is currently achieved by simple dilution of the aircraft plume at the altitude of injection, with no chemical changes taking place, into a 1° longitude by 1° latitude by 1 km altitude grid. Further scaling of the exhaust composition is required when models employ larger grid sizes, again with the same "frozen" chemistry assumption.

The Near-Field Interaction (NFI) component of the Subsonic Assessment (SASS) Program was established to critically examine aircraft plume and wake processes. Its objective is to determine whether any chemical or physical processes occurring in the complex fluid dynamics regime of an aircraft plume and wake can alter the properties of engine exhaust products or their deposition altitude in any way that necessitates modification of global model input assumptions.

The SASS NFI efforts follow naturally from ongoing investigations conducted within the NASA Atmospheric Effects of Stratospheric Aircraft (AESA) project [Stolarski and Wesoky, 1995]. Although substantial differences exist between subsonic and supersonic engine operating parameters and airframe structures, models developed for the supersonic case are directly applicable to the subsonic case. The existing state-of-the-art theoretical models developed within AESA have focused on the near-field regimes closest to the engine exit plane (< 20 km). Through the SASS NRA, several additional model efforts were initiated to examine chemistry and physics in the wake dispersion regime (> 20 km). In addition, several field instruments capable of measuring key gaseous and particle species in aircraft wakes were selected for development.

In order to further define and coordinate NFI activities within SASS and AESA, a Near-Field Interactions Workshop was held at the NASA Langley Research Center (LaRC) on August 22-23, 1994. In this chapter we summarize the results of that meeting. The workshop agenda and a list of attendees are contained in Appendix 4-1. The agenda for the workshop included:

- Presentations of currently funded theoretical modeling activities.

- Presentations of proposals for field measurements.

- Definition of the essential measurements required to evaluate wake/plume models.

- Discussion of appropriate instruments required to obtain those essential measurements.

- Discussion of the feasibility for a near-field experiment campaign.

Subsequent sections of this chapter address the last three items.

The recommendations of this workshop, which are summarized later this chapter, are actively being incorporated into SASS planning. The SUbsonic aircraft: Contrail and Cloud Effects Special Study (SUCCESS) mission, described in Section 7.2, will include several near-field objectives and will couple observations from both the DC-8 and Sabreliner aircraft platforms. One of the instruments developed for near-field detection of nitric acid (HNO_3) will be tested and utilized on both of the platforms. An additional activity named the SASS Near-Field Interaction Flight Experiment (SNIF) will combine ground-based lidar and Sabreliner-based *in situ* observations of a Boeing 737 plume in order to characterize the evolution of plume particulates and validate models of plume dynamics and chemistry. Finally, initial planning has begun on coordinating future near-field studies with the ER-2-based Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) campaign scheduled for 1997. Possible intercepts of an F-18, Concorde, or other aircraft are being contemplated.

ESSENTIAL PARAMETERS FOR EVALUATING AIRCRAFT WAKE/PLUME MODELS

The NFI component of the Atmospheric Effects of Aviation Program (AEAP) addresses the fact that the exhaust gases emitted by a transport aircraft undergo a number of complex interacting processes (e. g., chemical reactions and particle forming nucleation and condensation) as the hot engine exhaust plume interacts with the trailing wing-tip vortices and subsequently mixes with the ambient atmosphere. These processes occur in three physically identifiable regimes behind the aircraft. These regimes are: (1) the exhaust plume, (2) the wake vortex, and (3) the vortex break-up and wake dispersion regimes. The physical parameters characterizing these regimes will vary for specific aircraft and cruise conditions. The values shown in Table 4-1, calculated for a Boeing 707 aircraft cruising at 12.2 km altitude with an ambient atmospheric temperature of 217.3 K, are indicative of the conditions encountered in the near-field regimes of most subsonic commercial aircraft of interest.

Table 4-1. Near-Field Interaction Regimes*

	Exhaust Plume	Wake Vortex	Vortex Breakup and Wake Dispersion
Temperature range (K)	605 - 233	233 - 217.5	217.5 - 217.3
Dilution ratio (EG/TG)	1 - 25	25 - 1900	1900 - ...
Time since emission (s)	0 - 0.6	0.6 - 91	91 - ...
Distance behind plume (km)	0 - 0.14	0.14 - 22	22 - ...

* Calculated for a Boeing 707 at 12.2 km cruise altitude and 217.3 K ambient temperature. EG/TG = emitted gas divided by total gas

These near-field regimes are of interest because they contain far higher concentrations of reactive, exhaust-derived, chemical species families that are critical to a wide range of atmospheric chemical processes. The exhaust-enhanced chemical families of current interest are: (1) nitrogen oxides (NO_x and other NO_y species) that are active in ozone production and destruction reactions and the formation of polar stratospheric cloud (PSC) particles, (2) sulfur oxides (SO_x) that form chemically active and cloud/PSC-nucleating sulfuric acid (H_2SO_4) aerosols, and (3) hydrogen oxides (HO_x) that oxidize NO_x and SO_x species and participate in ozone photochemistry. In addition, these near-field regimes may also be rich in soot particles, small sulfuric acid/water particles and, in contrail-forming wakes, larger liquid water or ice particles all of which may serve as sites for heterogeneous reactions at rates higher than normally found in the upper troposphere or lower stratosphere. Finally, the conversion of NO_x to HNO_3 may allow formation of HNO_3/water ice particles in the vortex break-up and wake dispersion regime. Contrails and other wake particles may also play a role in the radiative properties and cloud condensation physics of the near-field and, of more potential importance, exhaust rich far-field regions.

The goals of the Near-Field Interaction Program are to: (1) assess the degree of chemical processing of key trace chemical families and the extent of new particle production, including cloud condensation nuclei (CCN) in the near-field regimes; and (2) to determine with the help of other components of the NASA AEAP if these processes change our understanding of the atmospheric impact predicted by current assessment models which distribute aircraft exhaust products to large atmospheric scales before computing their impact on atmospheric chemistry

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and radiative transfer. In order to achieve goal (1), the NASA AEAP has funded development of fluid dynamic/chemistry/microphysics models designed to predict the degree of near-field chemical processing and microphysical particle formation and activation for various aircraft/flight conditions of interest to the program. However, to build confidence in the accuracy and completeness of these models, it will be necessary to evaluate the model predictions with chemical, microphysical, and flow structure/property measurements in actual engine exhaust plumes, vortex wakes, and wake dispersion regions. The purpose of this section of the report is to define the observables and scenarios which should be included in an NFI measurement program.

Selection of Parameters to Be Measured

Currently, the NASA AEAP NFI models are being designed to address the chemical and physical processes shown in Table 4-2. The exhaust plume models focus on chemical processing, including: (1) NO_x oxidation by exhaust HO_x and entrained ambient ozone; (2) SO_x oxidation by exhaust HO_x and entrained and bypass atmospheric oxygen; (3) hydration of plume-formed H_2SO_4 vapor by exhaust water vapor; and (4) the activation of soot to CCN by plume-oxidant and acid gases. As the plume dilutes and cools, condensation processes commence, including the formation of additional aerosol through binary homogeneous nucleation and growth of existing aerosols through gaseous uptake. The wake vortex models, in which the rapidly cooling and less reactive far plume flows are entrained into the wing-induced vortex structure and continue chemical processing at a low level, concentrate on microphysical particle formation and/or activation processes. These processes include: (1) continuing binary homogeneous nucleation of H_2SO_4 and water vapors (which start in the exhaust plume regime); (2) coagulation of the resulting H_2SO_4/water nuclei; (3) interaction of soot particles with both non-nucleated H_2SO_4 hydrates and H_2SO_4/water nuclei; (4) the formation of activated soot and/or H_2SO_4 aerosol CCN; and (5) the condensation of water vapor on these CCN to form contrails. Finally, vortex break-up and wake dispersion regime models deal with microphysical, fluid dynamic, and photochemical processes in the exhaust-rich region, including: (1) photolysis of plume-produced nitrous acid (HONO) to produce the hydroxyl radical (OH); (2) the dispersal rate and spatial structure of the evolving wake dispersion regime; (3) the evaporation and/or formation of water and/or HNO_3 particles; and (4) the possible radiative cooling and subsidence of the water-vapor-rich and ozone-poor wake dispersion regime gases.

Table 4-2. Near-Field Chemical and Physical Processes

Exhaust Plume	Wake Vortex	Vortex Breakup and Wake Dispersion
NO_x oxidation to HONO and HNO_3	H_2SO_4/H_2O binary nucleation	HONO photolysis (OH production)
SO_2 oxidation to H_2SO_4	Acid nuclei coagulation	Contrail dispersion/ evaporation
H_2SO_4 hydration	Soot/acid and acid hydrate scavenging	Exhaust species dispersion
Soot oxidation/chemical activation	Soot/acid nuclei coagulation	PSC formation (?)
H_2SO_4/H_2O binary nucleation	CCN formation	Radiative cooling/subsidence (?)
	Contrail formation	

The critical parameters suggested by these near-field modeled processes are listed in Table 4-3 for each regime. Exhaust plume regime measurements should focus on the emission indices and evolving speciation of the NO_y, SO_x, and HO_x chemical families. It may not be feasible to measure the HO_x emission index directly; however, careful speciation of the NO_y and SO_x families in the far plume or wake vortex regimes should allow its back calculation. Plume soot properties, gas temperature, and exhaust concentration should also be measured to evaluate plume mixing models.

Table 4-3. Near-Field Observables

Exhaust Plume	Wake Vortex	Vortex Breakup and Wake Dispersion
NO_x emission index (NO_x/CO_2)	Exhaust plume measurements	Wake vortex measurements
SO_x emission index (SO_x/CO_2)	**+**	**+**
NO_y speciation (NO, NO_2, HONO, HNO_3)	H_2SO_4/H_2O condensation nuclei (number density, size distribution)	Photochemistry of exhaust rich region
SO_x speciation (SO_2, SO_3, H_2SO_4, $H_2SO_4 \cdot nH_2O$)	Contrail droplet properties (number density, size distribution, composition)	Particulate evolution
HO_x speciation (OH, HO_2, H_2O_2)	Contrail volume/shape	
Soot particulate properties (number density, size distribution, hydration properties)	Vorticity Turbulence scale	
Gas temperature profiles		
Exhaust concentration profiles		

Wake vortex regime measurements should include the same parameters measured in the plume, plus careful measurement of sulfuric acid/water nuclei and contrail droplet/particle properties as they are formed in the wake region. The dynamical structure predicted by these models can be tested by careful imagery and/or lidar profiling of the vortex structure and any exhaust detrainment as defined by soot and/or contrail particle distributions. Direct measurements of wake vorticity and turbulence scales may also be possible.

Finally, measurements in the vortex breakup and wake dispersion regime can encompass parameters from the first two regimes, as well as measurements of ongoing photochemical processes, such as OH production by HONO photolysis, and microphysical processes such as contrail particle growth or evaporation.

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Measurements/Experiments to Obtain Critical Parameters

Using Table 4-1 as a guide, the following categories of parameters are considered to be critical for evaluating NFI models:

1. Plume vortex characteristics
   - Entrainment/detrainment
   - Turbulence parameters
   - Background atmospheric parameters

Understanding the degree of entrainment of exhaust gases into the vortex produced behind the aircraft is important for predicting how these gases mix with the background atmosphere and the chemical evolution within the plume.

2. Oxidation of plume exhaust constituents to acid gases
   - NO_x to HNO_3 and $HONO$
   - SO_x to H_2SO_4

The formation of acid gases in the near-field exhaust facilitates the formation of aerosol particles and can alter the reactivity of new or pre-existing particles. These particles may alter gas phase constituents through surface reactions or sediment, carrying acids to lower altitudes.

3. Characterization of aerosols
   - New particle formation
   - Composition of aerosols
   - Aerosol particle growth
   - Rate of CCN formation and hydration properties

In addition to their role with acid gases noted above, aerosols participate in contrail and cloud formation and are radiatively active.

4. Mixing in the wake at vortex breakup
   - Scales of motion

The detailed breakup of the wake structure provides a strong test of the model simulations of the fluid dynamics processes.

In response to the need to assess these critical parameters, several options were discussed. The first option is collaboration with planned airborne sampling campaigns. With the limited resources of the NFI component of AEAP, a collaboration would optimize the science return for NFI objectives. In turn, the NFI component could contribute resources to the collaborating program. Two programs were considered:

1. SUCCESS

The SUCCESS campaign, which is discussed in more detail in Section 7.2, will use an extensive instrument complement on the NASA DC-8 aircraft to address a wide variety of chemical and aerosol effects of aircraft exhaust products. A detailed description of the science questions and

the payload is included in Appendix 4-2. Planned measurements of the DC-8 exhaust will necessarily be in the far field, but will reflect near-field processes. SUCCESS data may, therefore, be useful for constraining the near-field models. The scanning lidar observations may be able to explore the near field of another aircraft. For *in situ* sampling, the DC-8 could be operated behind another aircraft to obtain measurements over a range of distances. The DC-8 payload has been expanded to include more constituents, such as the Chemical Ionization Mass Spectrometer (CIMS) (Appendix 4-4D) or the Mobile Aerosol Sampling System (MASS) for aerosol properties (Appendix 4-4A). The DC-8 can also run different fuels through different engines in flight. Thus, fuels with different sulfur contents could be investigated. However, the DC-8 requires about 8 minutes to turn, so it could only sample its own plume with an effective 35 km separation.

2. NASA Sabreliner

A NASA Sabreliner is being prepared for an investigation of aerosol emissions and wake/plume characteristics as described in Appendix 4-3. Operation of this aircraft in its own wake would yield far field information just as described for the SUCCESS program. However, the Sabreliner could operate in the near to far field region of another aircraft. The contribution of NFI resources could augment this program and direct it toward NFI science goals. The addition of the MASS instrument as an option on the Sabreliner would expand the aerosol capability of this platform and connect any new results with those made with MASS on other airborne platforms and in ground-based tests.

Additional options to SUCCESS and the Sabreliner programs include airborne platforms with no specific wake sampling programs currently underway:

1. The NASA ER-2 platform has a comprehensive instrument complement for measurements of reactive and reservoir species and standard meteorological parameters (Appendix 4-5A). In recent airborne programs, the ER-2 has succeeded in sampling its own wake on several occasions. Key measurements have included reactive nitrogen and hydrogen species along with CO_2 to relate the observations to the quantity of fuel burned. Observations of condensation nuclei (CN) were also made in the wake. These measurements have provided a unique opportunity to compare with model calculations of dilution rates, hydrogen radical production, and reactive nitrogen partitioning in the far field. Further efforts could be undertaken with this aircraft in pursuit of another aircraft. (Editor's note: In October 1994, the ER-2 aircraft successfully intercepted the wake of a Concorde aircraft during supersonic cruise during the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE /MAESA) campaign [Fahey *et al.*, 1995]) The DC-8 may become a desirable choice based on the planned activities of SUCCESS.

2. An F-18 aircraft has been proposed as a sampling platform for the near-field region (Appendix 4-5B). Some studies are now underway to characterize aerosol properties of the GE-404 engines in new aircraft operating in ground-test facilities. An advantage of the F-18 is that closure could be achieved between ground-based and flight altitude conditions.

3. A WB-57F aircraft has recently been acquired by the National Center for Atmospheric Research (NCAR) Research Aviation Facility in Boulder, Colorado. This aircraft has a ceiling above 60,000 feet and can operate below that altitude without restriction. The payload is large (approximately 4000 lbs) and wing pods are possible. Proposals for instruments and programs are in progress. The Particle Analysis by Laser Mass Spectrometry (PALMS) instrument (Appendix 4-4C) has been funded under AESA for integration on the WB-57F.

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In addition to the above airborne platforms, other options for sampling aircraft wakes include the NASA LaRC ground-based lidar (Appendix 4-4B). This lidar has demonstrated the detection of a wake of known age from a known aircraft overflying the lidar site. Upgrade of the lidar to achieve better spatial resolution is underway. Critical tests of the fluid dynamics of the near-field region may be possible with the data from this system. There is a lidar capability at the Department of Energy Atmospheric Radiation Measurement (ARM) site in Oklahoma where the SUCCESS program is planned to operate, but no information on this lidar system was available at the workshop.

RECOMMENDATIONS

Several recommendations emerged from the discussions conducted at the workshop for consideration of the NFI program.

- Consider interaction with the SUCCESS program to establish collaborations to make efficient use of the NFI resources with a goal of using the data to constrain the wake/plume models.

- Consider how the Sabreliner could participate in SUCCESS by making additional measurements of the DC-8 wake. Consider what measurements could contribute to both the NFI and the SUCCESS goals.

- Consider how best to use the ground-based lidar to obtain measurements to constrain the wake/plume models and contribute to the NFI objectives.

- Consider the F-18 platform option.

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Stolarski, R. S., and H. L. Wesoky, Editors, *The Atmospheric Effects of Stratospheric Aircraft: A Fourth Program Report*, NASA Reference Publication 1359, Washington, DC, 1995.

ACKNOWLEDGMENTS

APPENDIX 4-1
NEAR-FIELD INTERACTIONS WORKSHOP AGENDA
22-23 August 1994
Hampton, Virginia

Monday, 22 August

8:15 am   Introduction and Workshop Charge - W. Grose (LaRC)

Wake/Plume Modeling Activities

8:30 am   R. Miake-Lye (Aerodyne)

9:00 am   T. Quackenbush (Continuum Dynamics)

9:30 am   S. Lewellen (West Virginia University)

10:00 am   S. Menon (Georgia Tech)

10:30 am   Break

10:45 am   O. Kandil (Old Dominion University)

Critical Parameters for Evaluating Wake/Plume Models

11:15 am   Open Discussion - Moderator - C. Kolb (Aerodyne)

12:30 pm   Lunch

2:00 pm   Open Discussion (continued) - Moderator - C. Kolb

Wake/Plume Measurement Activities

3:00 pm   B. Anderson (LaRC)

3:30 pm   E. Uthe (SRI)

4:00 pm   L. Poole (LaRC)

4:20 pm   Break

4:35 pm   P. Whitefield (University of Missouri, Rolla)

5:15 pm   S. Thorpe (Howard University)

6:15 pm   Dinner

8:00 pm   Continued Discussion/Writing

Tuesday, 23 August

8:15 am   B. Toon (ARC)

Measurements/Experiments to Obtain Critical Parameters

8:40 am   Open Discussion - Moderator - D. Fahey (NOAA)

10:15 am   Break

10:30 am   Open Discussion (continued) - Moderator - D. Fahey

12:00 Noon   Lunch

1:30 pm   Summary - Grose/Stolarski/Thompson/Wesoky

2:00 pm   Adjourn

Near-Field Interactions Workshop
Hampton, VA
22-23 August 1994

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APPENDIX 4-2

SUCCESS (SUbsonic aircraft: Contrail and Cloud Effects Special Study)

A. Questions for subsonics program related to climate

   .. What are the effects of contrails on the Earth's radiation budget?
  a. What fraction of the Earth is now covered by contrails?
  b. What are the meteorological and aircraft-related properties that lead to contrail formation?
  c. How do contrails spread to form cirrus sheets? Would these sheets have formed without aircraft, or are the aircraft responsible?
  d. Do aircraft flying through cirrus impact them either through contrail interactions or turbulence?
  e. What are the radiative properties of contrails - do they depend on altitude?
  f. Do contrails act as a significant source or sink of water vapor?

   2. Does aircraft exhaust affect ambient cirrus?
  a. What type of particles act as nuclei for cirrus cloud formation?
  b. Do aircraft emit special kinds of particles or gases that might affect ice formation?
  c. What are the size and number of sulfate particles in aircraft wakes?

   3. Do aircraft emit enough soot or sulfate to be radiatively significant?
  a. What is the optical depth, surface area, and composition of aerosols in the upper troposphere and lower stratosphere?
  b. How much soot, sulfate and other particles are emitted by aircraft?

   4. Do significant heterogeneous reactions occur in contrails or in cirrus that might affect the NO_x budget?
  a. What is the ratio of NO_x/NO_y in the exhaust that has been through a contrail versus that which has not gone through a contrail? Does the ratio vary between night and day?
  b. How much SO_2 is scavenged by cirrus clouds?
  c. Is NO_y present on cirrus cloud particles under some conditions?

B. Reasons for an aircraft flight program to study cirrus and contrails and the required measurements

   1. To ground truth satellite analyses of contrail and cirrus radiative properties.
  a. Cloud top and bottom altitude
  b. Cloud particle size and phase
  c. Scattering phase function
  d. Ice/water content
  e. Optical depth
  f. Homogeneity
  g. Transmission, reflectance, etc.

   2. To investigate mode of formation of cirrus clouds/contrails, predictability of cloud properties, persistence, spreading to form cirrus, and dissipation
  a. Ice nucleus concentration/composition
  b. CCN spectrum, CN
  c. Aerosol size spectrum
  d. Cloud particle size spectrum
  e. Large scale cooling rate, vertical velocity

f. turbulence
g. Water vapor concentration
h. Temperature profile
i. Aircraft tracers

3. To extend retrospective analyses of aerosol abundances and composition
   a. Aerosol composition
   b. Ice nucleus composition
   c. CCN, CN concentration
   d. Aerosol size distribution
   e. Aerosol optical depth

4. To investigate evidence for heterogeneous chemistry on contrails or on cirrus
   a. SO_2
   b. NO_x , NO_y , HNO_3
   c. Tracers/hydrocarbons

C. Strawman payload - DC-8 clouds and contrails

Instrument	PI	When Ready	Question Addressed	SASS Funded
Aerosol size	Pueschel	now	2c	no
Aerosol composition	Becker	2 yrs	3a, 2a	yes
CCN/Supersaturation	Hallett	1 yr	2b, 3c	yes
CCN/Supersaturation	Cooper	2 yrs	2b, 3c	yes
CN	Hallett	now	2b, 3c	yes
Ice particle size (replicator)	Hallett	now	1b, 2d	yes
Ice particle size, phase function	Lawson	1 yr	1b, c, f, 2d	yes
Ice water content (IWC)	Gerber	1 yr	1d	yes
Ice nuclei composition and IWC	Twohy	1 yr	2a, 1d, f	yes
Ice nuclei concentration	Kreidenweis	1 yr	2a, 3b	yes
Water vapor (diode)	Sachse	now	2g	no
Temperature, winds	Chan	2 yrs	2h	yes
Temperature profile	Gary	1 yr	2h	yes
Turbulence	Chan	2 yrs	2f	yes
NO_x , NO_y	Ridley	now	2i, 4b	no
HNO_3	Podolske	2 yrs	4b	no
CO, CO_2, CH_4, N_2O	Sachse	now	2i	no
Scanning lidar	Uthe	1 yr	1a, f	yes
Hydrocarbons	Blake	now	4c	no
(or PAN	Singh	now	4b	no
or OH)	Brune	2 yrs	4c	yes

D. ER-2 instrumentation

Instrument	PI	When Ready	Question Addressed	SASS Funded
Water vapor lidar	Browell	1 yr	2g	no
Cloud lidar	Spinhirne	now	1a	no
Broad band radiometers	Valero	now	1g	no
High spectral resolution radiometers (HIS)	Smith	now	1g	no
(Imager) MODIS simulator	King	now	1g	no

E. Ground-based systems

Instrument	PI	When Ready	Question Addressed	SASS Funded
Scanning lidar	Sassen	1 yr	1a , b, f	yes
	Eloranta	now	1a , f	no
Radiometers	ARM site	now	1g	no
Sondes	ARM site	now	2h	no
Profilers	ARM/NOAA	now	2e	no
Optical depth (better on low-altitude aircraft, Valero)	Russell	now	1e, 3e, 1f	no
Water vapor	Melfi	now	1g	no

Issues: Air traffic control, upwind boundary conditions, instrument conflicts on DC-8. Other aircraft that may participate (WB-57F, ARM unmanned aerial vehicles (UAVs)).

F. Ideas for missions using the DC-8/ER-2 to understand subsonic aircraft effects on clouds and radiation

Goals:
    A. Ground truth satellites
    B. Investigate mode of formation of cirrus and contrails
    C. Identify properties of aerosols in the upper troposphere
    D. Search for signs of heterogeneous chemistry

1. Based at Department of Energy Atmospheric Radiation Measurement/Clouds and Radiation Testbed (ARM/CART) site in Oklahoma for about 4-6 weeks at time of year when contrails are most common. Also need about 6 weeks to integrate instruments and do test flights.
2. Would probably require about 110 hours of DC-8 flight time (20 hours for three test flights, 12 hours of transit flights, 10 eight-hour flights in Oklahoma)
3. Structure of flights for the DC-8
    • Test flights up and down the coast of California. These flights will characterize the aerosols over the mid-latitudes of the Northern hemisphere as well. If flights are shorter than the eight hours assumed, then more could be made.

- Oklahoma flights (use another aircraft to create contrails to study).
  - Two flights north and south to characterize aerosols in air corridors and aircraft wakes.
  - Two flights along frontal systems to study cirrus properties.
  - Two flights above cart site in cirrus and imbedded contrails.
  - Two flights above cart site in cirrus and imbedded contrails.
  - Two flights above cart site in cirrus and imbedded contrails.
  - Two flights in contrails isolated from cirrus.
  - Two flights to make up for problems.

Appendix 4-3

Wake Plume Sampling by a Sabreliner: Airborne Investigation of Aircraft Aerosol Emissions and Wake/Plume Characteristics
B. Anderson, NASA LaRC

A. Objective - To investigate the following as a function of meteorology and aircraft type:

1. Emission ratio, size distribution, volatility, and growth rate of exhaust particulates;
2. Geometry, thermal dissipation, vorticity, dispersion rate, and exhaust trapping efficiency/detrainment rates of wake vortices;
3. Meteorological conditions leading to the formation of contrails and their physical characteristics;
4. Experience in plume sampling which might be useful for planning/conducting a more comprehensive experiment (e. g. collaborative experiment with DC-8);

B. Major Questions to be Addressed

1. How well do existing theoretical models predict aircraft wake/plume dynamics? Particle densities and formation rates?
2. What effect does the ambient flow have on wake breakup and dispersion?
3. How do wake/plume aerosol size distributions change with time as a function of background meteorology/aerosol loading?
4. What is the number density of sulfate particles in aircraft plumes? Soot? How does the ratio of soot to sulfate particles change with plume age?
5. What meteorological conditions lead to contrail formation? Do these conditions vary with background aerosol loading?
6. Do contrails act as a significant sink for water vapor?
7. What is the size distribution of contrail particles? How does this vary with the background meteorology/aerosol loading?
8. How significantly do wake vortex dynamics, aerosol emission ratios, and contrail forming properties vary for various different transport aircraft?

C. Instrumentation for the NASA Sabreliner

Position/time: Time latitude, longitude, pitch, roll, heading, vertical acceleration, pressure altitude, geometric altitude, angle of attack, angle of sideslip, true airspeed

Meteorological/dynamical: Horizontal winds, vertical winds, static pressure, total pressure, total air temperature, dew point, velocity, temperature and humidity fluctuations,

Chemical/particle: CO_2; ozone; aerosols (>3 nm, >10 nm, >20 nm, >40 nm); fine aerosols (0.1 to 3 μm); coarse aerosols (0.5 to 8 μm); precipitation particles; chemical ionization mass spectrometer (aerosol precursor gases).

Appendix 4-4

Experimental Instruments

A. Mobile Aerosol Sampling System (MASS) [Hagen *et al.*, 1994]
   Donald E. Hagen and Philip D. Whitefield
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Principle of Operation:

MASS, configured for real-time sampling, consists of a variable temperature, oven-heated inlet line coupled to two or more (maximum of 5) electric aerosol classifiers (EACs), a 100% relative humidity (RH) water saturator in series or parallel, and a PMS Instruments laser aerosol spectrometer (LAS). With this system, real-time total aerosol concentration, size distributions, and hydration (CN activation) data can be acquired for particles in the size range 0.007 to 20.0 micrometers. The maximum sampling rate is one hertz (Hz). System operation and data acquisition are computer supported, although one technician is generally required in attendance. Off-line samples are acquired using dilutable storage tanks, impactors, and electrostatic precipitators. The system operates off 28 V dc with a peak current of 16 amps. Previously, the system has been deployed for airborne sampling missions on the NCAR Sabreliner and the DLR Dassault Falcon 20E and for ground-based sampling projects at USAF Phillips Laboratory, McDonnell Douglas, and Pratt & Whitney. In addition, a completely automated configuration for use on the NASA F-18 research aircraft has been designed.

Flight Configuration Specifications:

   Detection limit - particle size 0.007 to 20.0 micrometers
   Particle soluble mass fraction - 0 to 100%
   Sample rate - 1 Hz
   Weight - 250 kg
   Max. Dimensions - width: two 19-inch racks ; height: 1.35 m

B. NASA LaRC Aerosol Research Branch Lidar
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Ground-based lidar measurements have been made at 532 and 1064 nm of exhaust particles produced during nighttime overflights by the LaRC Boeing 737 research aircraft operating at an altitude of 3.85 km. Double backscatter maxima indicating the presence of individual exhaust plumes (without contrail development) were detected near flight altitude at absolute and relative times which were consistent with local wind speeds and the spanwise distance between the aircraft engines. A distinct and statistically relative minimum in backscatter (below the estimated atmospheric background level) could be seen between the two maxima during several of the aircraft passes. Horizontal and vertical resolution of the data was too crude to allow quantitative estimation of particle properties or plume flow characteristics.

New lidar system components have been identified and ordered which should provide much higher horizontal and vertical resolution (down to 1.5 meters) in future data sets. Plans have been made to repeat the experiments pending the future availability of the 737 aircraft (or other aircraft).

C. Particle Analysis by Laser Mass Spectrometry (PALMS)
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Interest in analyzing volatile species in aerosol particles, particularly for large numbers of single particles, calls for an instrument that can provide chemical analysis of aerosols with minimal sample preparation. PALMS is a portable instrument that was developed to make in situ measurements of the composition of individual, sized particles with diameters between 0.2 and 10 μm. Particles enter the instrument through a differentially-pumped nozzle. They then pass through a continuous laser beam. The scattered light signal provides both size information and provides a trigger for a miniature excimer laser. Ions produced when the excimer laser beam strikes the particles are analyzed in a time of flight mass spectrometer to provide a complete mass spectrum for each aerosol particle. Analysis of volatile species is feasible because the measurement takes place less than 1 ms after the particle enters the instrument, and the particles never touch any surface. Signal-to-noise is excellent - often ~1000, even for submicron particles.

The PALMS instrument is currently funded for the WB-57F aircraft by the AESA component of NASA's High-Speed Research Program (HSRP).

D. Chemical Ionization Mass Spectrometer (CIMS)
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   Phillips Laboratory
   Hanscom Air Force Base, MA

Neutral mass spectrometry
   • CO_2
   • Others at close distance (> 0.01 to 0.1 ppmv when no interference)

Ion mass spectrometry
   • SO_x (SO_2, SO_3, H_2SO_4, ...)
   • NO_y (HNO_2, HNO_3, $ClONO_2$, possibly NO and NO_2)
   • Series of organic amines
   • Cl_y (HCl, HOCl, $ClONO_2$, possibly ClO)
   • At airplane speeds, wall losses are small (t ~ 0.01 to 0.1 s)

Preliminary measurements have been taken behind an F-15 aircraft engine in ground operation. Measurements onboard an aircraft are feasible.

Appendix 4-5

Aircraft Platforms

A. ER-2 Platform

This is the primary payload that was operational on the ER-2 aircraft during the ASHOE/MAESA field program in 1994. A subset of these measurements would be useful for far-wake sampling by the ER-2. (Editor's note: The ER-2 aircraft was successful in intercepting and sampling the wake of an Air France Concorde near New Zealand in October 1994 [see previous reference to Fahey *et al.*, 1995].)

	Technique	Institution
Tracer species		
N_2O	Tunable diode laser (TDL)	NASA Ames, JPL
CH_4	TDL	JPL
CFC-11, CFC-12, CFC-113, CH_3Cl, CCl_4, N_2O, CH_4	Gas chromatography (GC)	NOAA/CMDL
CO_2	Non-dispersive infrared (NDIR)	Harvard
Non-conserved/reservoir species		
O_3	UV photometer	NOAA/AL
H_2O	Lyman α hygrometer	NOAA/AL
HCl	TDL	JPL
NO_y	Catalysis chemiluminescence	NOAA/AL
CN, aerosols	Light-scattering spectrometer, impactor	U. Denver, NCAR, NASA Ames
Reactive species		
NO	Chemiluminescence	NOAA/AL
ClO, BrO	Titration/resonance fluorescence	Harvard
OH, HO_2	Titration/resonance fluorescence	Harvard
CO	TDL	JPL
Meteorological		
Pressure, temp. winds	A/C transducers	NASA Ames
Temperature profile	Radiometer	JPL
Radiation		
Photodissociative	UV-Visible spectrometer	AES (Canada)

B. F-18 Platform

The McDonnell Douglas F-18 aircraft has been proposed as a platform for use in near-field measurements. NASA has two such aircraft at the Dryden Flight Research Center. Some considerations in using the F-18 are:

- Low-cost, dedicated platform for collecting data on particulate emissions and soot/acid processing

- Ground-based measurements of particulate emissions currently in progress

- Ability to carry large payload of sampling instruments

- Ability to operate in the near field of subsonic (and, under some conditions, supersonic) aircraft

- Established telemetry capability

A possible payload for near-field aerosol measurements might include: Mobile Aerosol Sampling System (MASS), University of Missouri; CO_2 by infrared (IR) absorption, DLR, Germany; H_2O by diode laser absorption, Physical Sciences Inc.; Chemical Ionization Mass Spectrometry (CIMS), Phillips Laboratory; and an IR camera, Aerospace Corporation.

Chapter 5

Kinetics - Data Panel Reports

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PREAMBLE

Laboratory studies are fundamental to all other elements of the Subsonic Assessment (SASS) Project; they provide the basic photochemical input data for the models, which are then tested against observations of the real atmosphere. Objectives for the laboratory studies identified in the initial SASS program plan include: identify chemical processes for gas, liquid, and solid phases that are affected by aircraft emissions; perform laboratory investigations of single and multiphase chemical reaction rates, absorption cross sections at photolytic wavelengths, and other properties under simulated atmospheric conditions; issue (in association with the Upper Atmosphere Research Program (UARP)) periodic Kinetics Data Panel reports to standardize input for chemical modeling; and prepare standards for instrument calibration and intercomparisons as needed.

While the needs of the modeling activity are the primary driver for laboratory studies, such guidance was not available in the initial formulation of the SASS Laboratory Studies subelement. Instead, the laboratory studies activity was developed based on competitive peer review (scientific merit as well as relevance to SASS) of proposals submitted in response to the NASA Research Announcement (NRA). In addition to the other SASS areas, the NRA requested laboratory studies proposals encompassing five major areas:

(1) homogeneous kinetics, with special emphasis on the pressures and temperatures encountered in the lower stratosphere/upper troposphere;
(2) heterogeneous chemistry, including reactions on various forms of sulfate aerosols, ice, and soot;
(3) condensed-phase (aqueous) chemistry;
(4) spectroscopic studies relevant to field instruments; and
(5) the physics of particle formation.

The laboratory studies effort includes both bulk-phase and single-particle studies. In the future, areas of emphasis in the laboratory program will be prioritized and redirected based on the results from field campaigns and modeling studies, coupled with the Kinetics Data Evaluations. Individual laboratory projects are described in the Appendix. Some of these build on studies underway in the UARP or the Atmospheric Effects of Stratospheric Aircraft (AESA) component of the High-Speed Research Program (HSRP), while others are new to the NASA atmospheric chemistry programs.

Input data for photochemical models needs to be provided as a comprehensive set of consistent, critically evaluated data. In the early days of the UARP, a NASA Kinetics Data Panel was formed to provide such an evaluation, and has done so on a biennial basis (the latest being in 1994 [DeMore et al., 1994]). The initial stratospheric focus of that Panel has expanded over the years, and includes a large number of "tropospheric" processes. For SASS, the Panel will expand its reviews to encompass the upper tropospheric needs of the SASS Project. The decision to augment the existing activity, rather than initiate a separate one, was based on the recognition that:

(1) Distinction between the upper troposphere and lower stratosphere is largely artificial.

(2) Resource considerations, time, and cost of the data evaluation process preclude an effort that would duplicate much of the stratospheric evaluation.

(3) Other kinetics panels (e. g., the International Union of Pure and Applied Chemistry (IUPAC)) are performing evaluations of organic gas-phase and heterogeneous reactions, and their evaluations can be incorporated by the NASA Panel as appropriate.

While the current Panel reports are generally adequate for most gas-phase upper tropospheric chemistry, they are not complete for hydrocarbon oxidation (especially above C_2). Also, heterogeneous processes in the stratosphere are well-covered, although aircraft-specific aerosols and upper tropospheric aerosol chemistry are not. Additionally, condensed-phase (aqueous) reactions are not included in the present evaluations. To better determine how the Data Panel could meet the needs of SASS, a series of workshops were held, and reports were prepared by Dr. John Herron of the National Institute of Standards and Technology (NIST). Those three reports are included as subchapters here. In his first report to the NASA Data Panel, Dr. Herron reviewed engine emissions, gas-phase reactions, aerosol reactions, and aqueous-phase reactions that are relevant to aircraft effects. This report included the responses from nine members of the atmospheric science community, principally modelers, who were consulted for their views on the data needs for assessment of aircraft effects. On the basis of these queries and studies, a draft report was presented to the NASA Data Panel at a meeting on 3-4 March 1994. Preliminary recommendations which were made to the Panel included:

(a) continued emphasis on heterogeneous chemistry,
(b) extension of the database through C_3 hydrocarbons,
(c) development of a lumped parameter approach for C_4 hydrocarbons and beyond, and
(d) extension of Panel evaluations to include aqueous phase chemistry.

To further refine and discuss these recommendations, a meeting of additional experts was convened in Washington, DC, on 5-6 May 1994. This meeting was attended by several tropospheric scientists (see List of Attendees), and the recommendations of the Herron report were discussed in detail. On this basis, a modified set of recommendations was presented to the Data Panel on 12-13 May 1994, and the Panel adopted the following approach for meeting the SASS data requirements:

(1) Maintain and, as required, expand the current emphasis on heterogeneous chemistry as it applies to the troposphere.

(2) Extend the database to include the full tropospheric chemistry cycle through C_3 hydrocarbons, including their oxidation products and all possible nitrogen-containing products. Initiate this project by co-opting the IUPAC evaluation.

(3) Evaluate and, as necessary, develop a lumped parameter approach to handle all hydrocarbons beyond C_3, using generic nonmethane hydrocarbons (NMHCs).

(4) Include aqueous atmospheric chemistry in the Panel evaluations.

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The Panel approach to meeting these recommendations is as follows: Items (1) and (2) will be accomplished by the present Panel members, as a continuation and extension of current evaluation practices; item (3) will begin with a survey by Dr. Herron of existing methods to determine which, if any, are suitable for the present needs; and item (4) will be met by the addition of a new member to the Data Panel who is a recognized expert in the field of aqueous atmospheric chemistry. Several candidates for this appointment were nominated. At a Panel meeting on 13-14 May 1995, Dr. R. E. Huie was selected as the most appropriate candidate and has agreed to join the Panel as the member responsible for aqueous atmospheric chemistry. This expansion of the Data Panel activities was not included in the 1994 evaluation, but will be discussed in the upcoming 1996 evaluation.

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Section 5.1

Recommendations for Data Evaluation for Tropospheric Chemistry

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INTRODUCTION

This report is in response to the Laboratory Studies element in the NASA Research Announcement (NRA) *Atmospheric Effects of Aviation/Subsonic Assessment: Modeling, Data Analysis and Measurements in Support of the Advanced Subsonic Technology Program*, NRA 94-OA-01, dated 15 October 1993. Specifically, the announcement raised the following questions with regard to laboratory programs and the parallel activity in data evaluation:

- How well are rate constants for gas-phase reactions known for upper troposphere/lower stratosphere (UT/LS) conditions? How do uncertainties in these rates affect simulations of trace gas distributions influenced by subsonic aircraft emissions?

- How important are heterogeneous reactions to subsonic emissions? What is the importance of reactions on polar stratospheric clouds (PSCs) for subsonic emissions?

- Do reactions of emitted gases in the lower stratosphere that take place on particles result in transforming the gases?

- What is the effect if particles are transported between the stratosphere and troposphere?

- What is the interaction of aircraft emissions with the background aerosol? Do the emitted gases modify the nature (i.e., size, composition, shape) of the background aerosol?

- Do processes inside clouds (liquid phase) affect the fate of emissions from subsonics?

- Are the net effects on photodissociation rates known?

The starting point for this activity was stated by Dan Albritton in his summary remarks at the Workshop on Research Needs for a NASA Program on the Atmospheric Effects of Subsonic Aircraft held in Alexandria, Virginia, 29-30 April 1993:

> The emissions of subsonic aircraft are potentially linked with two environmental issues that are currently on the minds of governments:
>
> - *stratospheric ozone depletion*, via NO_x and other aircraft emissions reaching the lower stratosphere; and
>
> - *global warming*, via the NO_x-catalyzed formation of greenhouse ozone in the upper atmosphere, the increase of H_2O abundances in the vicinity of the tropopause, and the formation of contrails and the influence on clouds.

This later was succinctly reduced to:

> A given fleet of subsonic aircraft yields what stratospheric ozone depletion and climatic perturbation?

The key issues are:

- What kinds and amounts of emissions can be expected from a fleet of commercial subsonic aircraft over the range of their operating conditions?

- Will these emissions significantly alter the existing atmospheric burden of the emitted compounds or of other atmospheric constituents?

- And, if they do, will this have consequences with respect to the two key issues noted above by Albritton?

Albritton made another very important point relevant to any program on subsonic aircraft emissions; namely that trying to address all of the problems of tropospheric chemistry is a hopeless task, the need here is to keep tightly focussed on those technical issues which can contribute to the resolution of policy issues, making use wherever possible of our existing knowledge base.

At the workshop and in subsequent discussions [Thompson and Hampson, 1993], a series of issues were raised which can provide a starting point for addressing the key issue for the Data Panel - What new chemistries (if any) should be included in the NASA Panel for Data Evaluation Recommendations to address the problem of subsonic aircraft?

Specific points raised at the workshop were:

- Does emitted water vapor in the form of contrails have any effect?

- Do emitted particulate serve as condensation nuclei for ambient and engine emissions?

- Do we need data to lower temperatures for gas? aerosol kinetics?

- Do we need better data for gas phase reactions as a function of pressure?

- Do we need to understand aerosol chemistry better? Are photochemical processes important? Are the surfaces used in laboratory studies relevant to the real atmosphere?

- Are there reactive species not now in the database that should be included?

- Do we need to incorporate aspects of aqueous chemistry?

- Do we need to understand wake chemistry in order to correctly arrive at the correct partitioning of nitrogen containing emissions?

- Does emitted sulfur play any role?

In addition, the following topics were raised at the workshop and noted in the summary [Thompson and Hampson, 1993]: PAN formation and destruction; oxidation schemes for CH_4, CH_2O, C_3H_8; nonmethane HCs; peroxy radical compounds; photolysis rates, 290-400 nm; and reactions in sulfuric acid (H_2SO_4).

For the Data Panel, the most important question is whether the database needs to be expanded to include global tropospheric chemistry. Subsonic aircraft fly at cruise altitudes in both the troposphere and the stratosphere. In northern latitudes, where much of the existing air traffic is concentrated, flights are about equally divided between troposphere and stratosphere, as shown in Table 5.1-1.

Stratospheric effects still can be rationalized within the existing framework of stratospheric chemistry, even if heterogeneous processes are not yet fully incorporated, or if new "surprises"

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Table 5.1-1. Estimates of percentage of fuel burn in the stratosphere for the subsonic fleet [WMO, 1992].

Month	Cruise Altitude = 10 km		Cruise Altitude = 11 km	
	Latitude of tropopause *λ_T at 10 km (°N)	Portion of Northern Hemisphere fuel burn that occurs in the stratosphere (percent)	Latitude of tropopause *λ_T at 11 km (°N)	Portion of Northern Hemisphere fuel burn that occurs in the stratosphere (percent)
January	38	56	33	72
February	42	41	33	72
March	43	40	34	72
April	46	27	35	72
May	47	26	40	56
June	55	16	45	40
July	65	2	55	16
August	65	2	55	16
September	64	2	50	26
October	58	8	45	40
November	52	16	45	40
December	49	27	40	56
Annual[†]		22		48

come along. The troposphere presents a different problem since the effects of subsonic aircraft within the troposphere are to modify tropospheric levels of gases and aerosols which may have a direct bearing on ozone or climate, but also which modify levels of other constituents which are transported to the stratosphere. For example, changing NO_x affects O_3 and consequently OH, which in turn, changes the "cleansing power" of the troposphere.

This report brings together conclusions and recommendations from earlier NASA and WMO reports and additional comments and suggestions from members of the active research community involved in laboratory measurement, atmospheric observations, and atmospheric modeling. Appendix 5.1-1. lists the workers consulted. Their comments are not specifically cited in the text.

In her letter dated 6 May 1993, Anne Thompson stated to attendees of the Subsonics Workshop: "The Workshop gave a green light for moving as quickly as possible to obtain a 'Recommendation for Lower Atmosphere Kinetics' that will support modeling for the next UNEP/WMO International Ozone Assessment."

ENGINE EMISSIONS

Gas-phase

There are limited data on emission levels of current or proposed new high-efficiency subsonic aircraft. Spicer *et al.* [1992] have reported data on military turbine engines. Table 5.1-2, taken from their work, gives data for emissions from test engines at ground level, at different power levels.

Methane is always the predominant organic species from aircraft fuel burn. However, since neither is present in ambient air (which is oxidized by passage through the engine), it is not clear whether aircraft are a net source or sink for atmospheric methane. The "nonmethane" organic compounds are either combustion products or unburnt fuel. The predominance of one or the other emitted species depends on the operating mode of the engine, but in general, the most important ones are C_2H_2, C_2H_4, HCHO, CH_3CHO, CH_3COCH_3, and a range of C_5 and greater alkanes.

Derived emission factors (grams of emitted substance to kilograms of fuel) at 63% thrust for the F110 engine are given in Table 5.1-3. They can be compared with the Boeing [1990] estimates, which also are shown in the table.

The partitioning of the nitrogen containing emissions is of great importance. This is not simply a function of engine temperature, but also of wake chemistry. Radicals, either as engine emissions or as background atmospheric constituents, convert NO to NO_2, HONO, HNO_3, etc.; the same is true with respect to SO_2 emissions. Under fuel-rich conditions, organic radicals will be even more prevalent and able to drive the NO oxidation reactions.

Under cruise conditions, hydrocarbons and their partial oxidation products will probably be emitted at very low levels, and the focus should be on water, nitrogen containing compounds, sulfur containing compounds, aerosols, and condensation nuclei.

This conclusion is supported by recent modeling studies [Beck *et al.*, 1992] in which it was found that the key parameter leading to enhanced levels of O_3 and OH was the amount of NO_x emitted. There was no significant difference found when hydrocarbon emissions were included in the model. However, the role of SO_2 in forming condensation nuclei or the chemistry taking place in condensation trails was not addressed in this study.

Aerosols

In a report to the Air Force, Spicer *et al.* [1990] give data on emissions of particulates. They note that the amount of emission is strongly dependent on the engine; the F110, for example, being much "cleaner" than the F101. Most particles emitted are smaller than 0.2 micrometer. For all engines the total particulate emissions are low; typical emission rates being about 5 x 10^5 particle cm^{-3}. Although these may be classified as "soots", their chemical nature may be complex.

From studies of atmospheric aerosols in the north Atlantic (lower stratosphere) [Stolarski and Wesoky, 1993], one can get some idea as to the size distribution of the atmospheric burden of "black carbon" aerosols. This is shown in Figure 5.1-1. However, if representative of engine emitted particles, it refers to aged rather than nascent populations. One notes that the population is concentrated in the less-than-0.2-micrometer range, in agreement with the emission data of Spicer *et al.* [1990].

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Table 5.1-2. Organic emissions from F110 engines with JP4 fuel [Spicer *et al.*, 1992].

Organic Species	Idle	30%	63%	Intermediate [a]
Methane	1.766	1.462	1.098	0.674
Ethane	0.033	0.022	0.024	0.013
Ethene	0.497	0.089	0.127	0.230
Propane	0.026	0.023	0.009	0.005
Acetylene	0.208	0.020	0.011	0.007
Propene	0.082	0.017	0.022	0.048
1-Butene - 1,3-Butadiene	0.034	0.016	0.016	0.009
1-Pentene	0.006	0.002	0.003	0.001
C5-ene	0.001	<0.001	<0.001	<0.001
n-Pentane	0.011	0.012	0.005	0.001
C5-ene	<0.001	<0.001	<0.001	<0.001
C5-ene	<0.001	<0.001	<0.001	<0.001
2-Methylpentane	0.009	0.021	0.008	0.001
3-Methylpentane	0.008	0.012	0.004	0.001
1-Hexene	0.003	0.004	0.005	0.002
n-Hexane	0.018	0.032	0.008	0.004
Methylcyclopentane - unk	0.010	0.018	0.005	0.002
Benzene	0.079	0.023	0.017	0.011
2-Methylhexane	0.005	0.011	0.002	<0.001
3-Methylhexane	0.017	0.019	0.012	0.009
n-Heptane	0.013	0.028	0.005	0.002
Methylcyclohexane	0.016	0.034	0.006	0.002
Toluene	0.985	0.032	0.012	0.007
2-Methylheptane	0.008	0.011	0.001	<0.001
3-Methylheptane	0.000	0.009	0.008	0.007
n-Octane	0.010	0.023	0.004	<0.001
Ethylbenzene	0.024	0.006	0.002	0.001
n-p-Xylene	0.086	0.021	0.006	0.003
Styrene	0.005	0.009	0.002	<0.001
o-Xylene	0.030	0.007	0.002	0.001
n-Nonane	0.015	0.025	0.002	<0.001
p-Ethyltoluene	0.007	0.007	0.002	0.001
1,2,4-Trimethylbenzene	0.015	0.013	0.002	0.001
n-Decane	0.025	0.033	0.002	0.001
Methylbenzaldehyde-ClOH14	0.006	0.007	0.001	<0.001
Undecane	0.021	0.022	0.002	0.001
Naphthalene	0.005	0.002	0.000	<0.001
Dodecane	0.019	0.015	0.002	0.001
Tridecane	0.037	0.017	0.004	0.001
Tetradecane	0.007	0.029	0.007	0.004
Formaldehyde	0.305	0.162	0.095	0.090
Acetaldeyde	0.140	0.080	0.042	0.032
Acrolein	0.015	<0.001	0.009	0.003
Propanaldehyde	0.066	0.012	<0.001	<0.001
Acetone	0.060	0.072	0.084	0.024
Benzaldehyde	<0.001	<0.001	<0.001	<0.001
Clyoxal	0.064	<0.001	0.004	0.016
Methylglyoxal	0.051	0.003	0.012	0.018
Biacetyl	<0.001	<0.001	<0.001	<0.001
TOTAL IDENTIFIED SPECIES	4.848	2.485	1.695	1.235
TOTAL ORGANIC COMPOUND CONCENTRATION	6.840	3.440	2.090	1.500

[a] Concentrations in ppmC (parts per million carbon; to convert to ppm by volume, divide by the number of carbon atoms).

Table 5.1-3. Aircraft emission factors (grams of emitted substance to kilograms of fuel used).

[Spicer *et al.* 1992]		[Boeing, 1990]	
Species	Emission Index	Species	Emission Index
Organic compounds	0.19	Hydrocarbons (as CH_4)	0.56
CO	1.6	CO	3.3
CO_2	4473	CO_2	3160
NO_x (as NO_2)	20.1	NO_x (as NO_2)	14.4
NO_2	1.0		
		SO_2	1.1
		H_2O	1230

## REACTIONS IN THE GAS PHASE

The current NASA database includes reactions for the nonhalogenated organic compounds CH_4, C_2H_6, C_3H_8, C_2H_2, C_2H_4, HCHO, CH_3OH, C_2H_5OH, CH_3CHO, CH_3OOH, HC(O)OH, and $CH_3C(O)OH$.

Although, there is a vast body of data available on atmospheric levels of trace atmospheric constituents near the boundary layer, and in particular within urban airsheds, there are fewer data available giving the vertical distribution up to and/or through the tropopause. Some of that information has appeared in the literature, but some may remain unpublished. These data are useful in making reasoned choices for adding new reactions to the database. Table 5.1-4 lists data from several sources, not necessarily compatible, but adequate to give a qualitative picture of which trace constituents are important in the upper troposphere.

Data for the lower troposphere are given in Table 5.1-5.

To a first approximation, the ordering of concentration levels near the tropopause is:

$$CH_4 > C_2H_6 > C_2H_4 \text{ and } C_3H_6 > C_3H_8 > C_4 \text{ and } C_5 \text{ alkanes} > C_2H_2 > PAN.$$
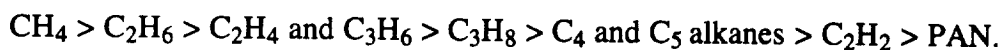
The levels reported for the lower troposphere indicate that other alkanes are probably present at much lower levels.

Aside from considerations of which reactive species and product offspring might be included in a tropospheric database, there is also the question of how to properly represent the temperature and pressure dependence of their reaction rate constants. Although the DeMore *et al.* [1992] and Atkinson *et al.* [1992] evaluation projects use essentially the same format, the problem of extrapolating data as low as 185 K should not be ignored.
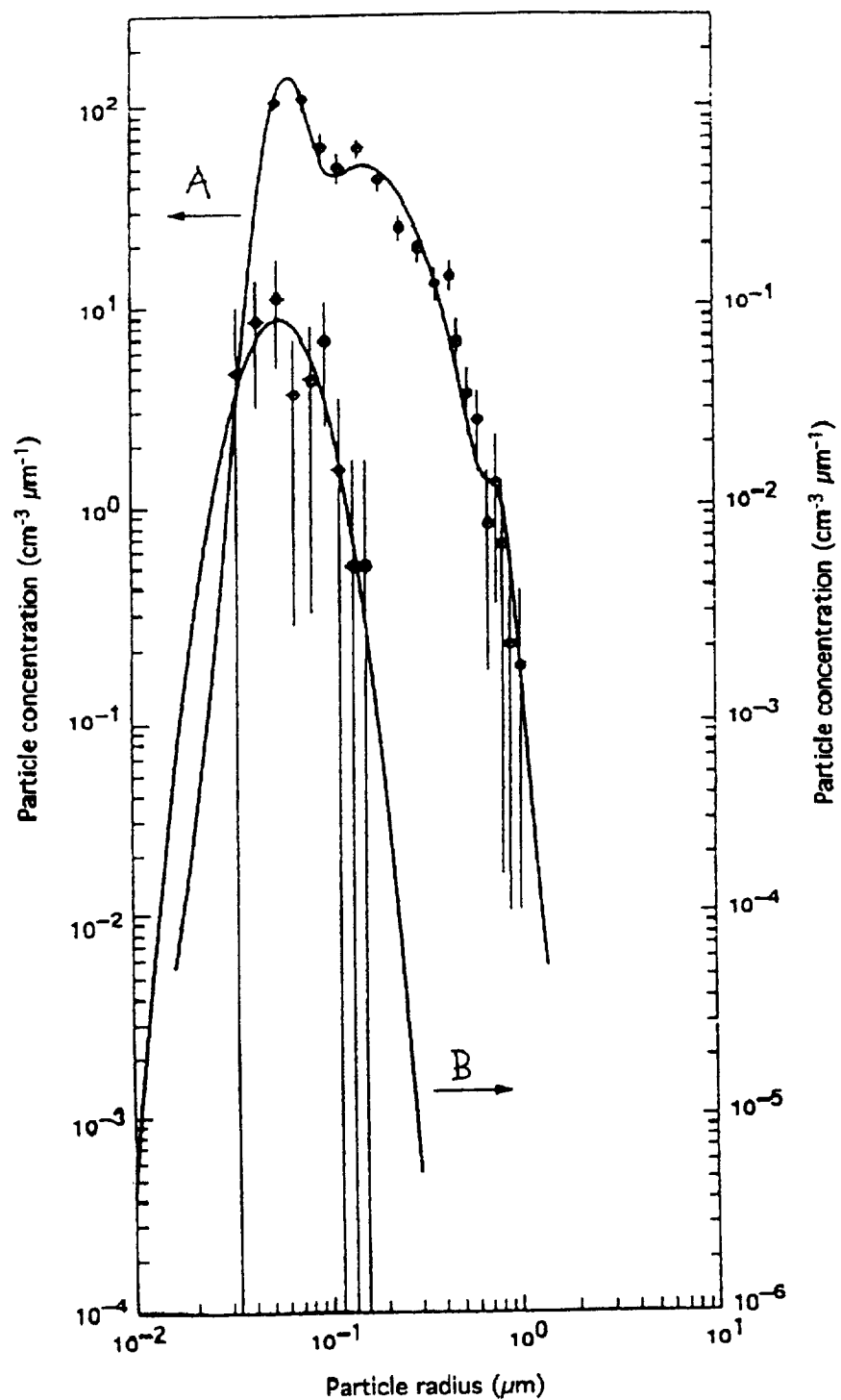
Figure 5.1-1. Aerosol size distribution for black carbon (B) and sulfuric acid aerosols (A),17 February 1992, near 52°N, 11.5 km MSL altitude [Stolarski and Wesoky, 1993].

Table 5.1-4. Levels of trace constituents of the upper troposphere.

Species	Range, pptv	Source
CH_4	2×10^6	Law and Pyle [1993b]
C_2H_6	1000 to 2000	Stolarski and Wesoky [1993]; Rudolph [1988]; Law and Pyle [1993b]
C_3H_8	300 to 500	Stolarski and Wesoky [1993]; Rudolph [1988]
$n\text{-}C_4H_{10}$	50 to 200	Stolarski and Wesoky [1993]; Rudolph [1988]; Law and Pyle [1993b]
$i\text{-}C_4H_{10}$	10 to 100	Stolarski and Wesoky [1993]; Rudolph [1988]
$n\text{-}C_5H_{12}$	10-400	Rudolph [1988]
$i\text{-}C_5H_{12}$	5 to 500	Rudolph [1988]
C_2H_4	100 to 2000	Rudolph [1988]
C_3H_6	100 to 1000	Rudolph [1988]
C_2H_2	100 to 400	Stolarski and Wesoky [1993]; Rudolph [1988]
PAN, $CH_3C(O)OONO_2$	10 to 300	Singh et al. [1993]; Rudolph et al. [1987]; Law and Pyle [1993a]
NO_y	1000 to 2000	Singh et al. [1993]; Murphy et al. [1993]

For-well studied reactions, the DeMore et al. [1992] and Atkinson et al. [1992] representations give much the same answers in deriving a rate constant outside the range of measurement. For example, the rate constant for the reaction OH + SO2, at 190 K, [M] = 1 x 10^{19} molecule cm-3 is calculated to be 1.29 x 10^{-12} cm3 molecule-1 s-1 from DeMore et al. [1992], and 1.19 x 10^{-12} cm3 molecule-1 s-1 from Atkinson et al. [1992], based on essentially the same data.

REACTIONS ON/IN AEROSOLS

The current NASA database contains data under the headings of mass accommodation coefficients, surface reaction probabilities, and solubility data.

Although the impetus for including these kinds of data in the panel report was polar ozone depletion, there is no reason to believe that the same processes are not relevant to the cold regions of the troposphere. The modeling studies on the effects of aircraft emission noted above do not allow for heterogeneous chemistry, but heterogeneous chemistry almost certainly will be included in future work.

Since heterogeneous chemistry is an active research area, it is not yet possible to develop a long range plan for data. The best approach is that in place; compile and evaluate everything.

Table 5.1-5. Levels of trace constituents of the lower troposphere.

Species	Range, pptv	Source
C_2H_6	1000 to 2000	Penkett *et al.* [1993]
C_3H_8	500	"
n-C_4H_{10}	200	"
i-C_4H_{10}	100	"
n-C_5H_{12}	75	"
i-C_5H_{12}	100	"
n-C_6H_{14}	40	"
n-C_7H_{16}	30	"
C_2H_2	400	"
Benzene	150	"
Toluene	75	"
$C_2H_5ONO_2$	1 to 5	Atlas *et al.* [1993]
1-$C_3H_7ONO_2$	1 to 5	"
2-$C_3H_7ONO_2$	2 to 8	"
n-$C_4H_9ONO_2$	0.1 to 0.5	"
(2+i)-$C_4H_9ONO_2$	2 to 5	"
i-$C_5H_{11}ONO_2$	0.1 to 0.5	"
$RONO_2$>2 Carbon atoms	5 to 20	"

REACTIONS IN THE AQUEOUS PHASE

For our purposes, we can define aqueous chemistry as processes taking place in droplets (about 10 micrometer diameter) of liquid water containing various amounts and kinds of trace atmospheric constituents. The droplets are formed around pre-existing aerosols into which other gaseous atmospheric constituents may dissolve. There has been considerable activity in this area because of the interest in fog and cloud chemistry [Lelieveld and Crutzen, 1990; Warneck, 1992].

From modeling studies, Lelieveld and Crutzen [1990] concluded that cloud chemistry played a significant role in determining levels of O_3, NO_x, and HO_x in the global troposphere. They suggested that, "advanced global-scale tropospheric chemistry models requires development of routines that properly simulate cloud occurrence and cloud chemistry."

INPUT OF RESEARCH COMMUNITY

Based on conversations with atmospheric scientists (see Appendix 5.1-1.), there was a general consensus that the database should be expanded to include tropospheric chemistry. However, the degree to which it should be expanded varied. This probably reflects the particular focus of the person queried.

At a minimum it was felt that for the simple organic species, up to two carbon atoms, the database should provide a complete scheme including PAN or other nitrogen containing organics. Extension to the C3s and C4s was the next level of complexity. These would include unsaturated compounds and oxygen containing products and intermediates.

The next level of complexity involves inclusion of aqueous chemistry. This is a necessary component of a global atmospheric model.

There was a clear consensus that heterogeneous processes must have very high priority in experimental programs. The need to work at temperatures down to 190 K using realistic surfaces was stressed by some workers.

The study of kinetics and mechanisms of gas phase reactions at low temperatures was also targeted as critical.

SUMMARY AND RECOMMENDATIONS

The basic question for consideration of the Data Panel is - What new chemistries, if any, should be included in the NASA Panel for Data Evaluation Recommendations to address the problem of subsonic aircraft?

In the absence of *in situ* emissions measurements contradicting the predictions of the engine community regarding engine emissions under cruise conditions, the only emissions that could affect atmospheric chemistry are NO_x, H_2O, SO_2 (depending on fuel composition), and possibly, soot type particulates.

In the stratosphere these emissions are already included in the database, and aerosol chemistry is an active research area whose results will be included in future database activities.

In the troposphere, the situation is not so simple. The emitted gas and aerosols are in the presence of a background of hydrocarbons, organic oxygen and nitrogen compounds, radicals, liquid and solid water.

In order to quantify the role of engine emissions in modifying levels of ozone, hydroxy, etc. in the troposphere, it may be necessary to include additional tropospheric chemistry.

However, the addition of new reactive species has to be approached conservatively. The approximate ordering of species concentrations in the upper troposphere, i.e., $CH_4 > C_2H_6 > C_2H_4$ and $C_3H_6 > C_3H_8 > C_4$ and C_5 alkanes $>C_2H_2 > PAN$, suggests that for each of the hydrocarbons, at least through C3, a complete reaction scheme be developed including all possible oxygen and nitrogen containing products. The DeMore *et al.* [1992] evaluation already includes many of these reactions; others,including sulfur containing ones, are in the Atkinson *et al.* [1992] evaluation. It might be wiser, at least initially, to co-opt the IUPAC database, to the degree possible, or at least use it as a starting point.

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Wake chemistry may also turn out to be important, since the conversion of emitted SO_2, NO_x, and H_2O in the wake leading to enhanced aerosol formation may be significant. This may have to await the evaluation of the importance of heterogeneous chemistry in the upper troposphere.

For aerosol chemistry, one can expect that processes active in the stratosphere will apply also to the troposphere. However, since aircraft fly at lower latitudes, photochemistry will need to be given much more attention. Also, the role of higher pressure will need to be accounted for.

Aqueous chemistry would represent a new area for the kinetics panel that would almost certainly require addition of new expertise. This is an area in which IUPAC is mounting a new project. The focus will be on the global troposphere, but it is not clear at present as to how much that activity will support NASA goals. Recent modeling efforts [Lelieveld and Crutzen, 1990; Warneck, 1992; Jacob, 1986; Moller and Mauersberger, 1992; Faust and Allen, 1992] provide reaction lists useful in starting work in this area.

It is worthwhile to repeat Albritton's warning that trying to address all of the problems of tropospheric chemistry is a hopeless task, the need here is to keep tightly focussed on those technical issues which can contribute to the resolution of policy issues, making use wherever possible of our existing knowledge base.

The conclusions of this report were discussed at a meeting of the NASA Data Panel in Boulder, CO on 3-4 March 1994, at a meeting on data needs for SASS held 5-6 May 1994 in Washington, DC, and at a second meeting of the NASA Data Panel in Boulder on 12-13 May 1994.

The recommendations for action that follow are basically those of the author, with some reordering of priorities based on the above discussions, and the addition by the NASA Data Panel of the recommendation on development of estimation methods for larger organic compounds:

1. Maintain and, as required, expand the current emphasis on heterogeneous chemistry as it applies to the troposphere. This is an active research area in which new phenomena can be expected to be discovered.

2. Initiate a new activity on aqueous chemical kinetics.

3. Extend the database to include the full tropospheric chemistry cycle through the C3 hydrocarbons, including their oxidation products and all possible nitrogen containing products.

4. For hydrocarbons larger than C3, develop empirical and/or theoretical methods for the direct estimation of the kinetics of reactions of the larger organic compounds in the atmosphere.

ACKNOWLEDGEMENTS

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Appendix 5.1-1

List of Workers Consulted

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Guy Brasseur, National Center for Atmospheric Research
Bruce Gay, Environmental Protection Agency
Charles Kolb, Aerodyne Research, Inc.
Jennifer Logan, Harvard University
Michael Prather, University of California, Irvine
Jose Rodriguez, Atmospheric and Environmental Research, Inc.
Susan Solomon, National Oceanic and Atmospheric Administration Aeronomy Laboratory
Donald Wuebbles, University of Illinois

Section 5.2

Recommendations for Data Evaluation for Tropospheric Chemistry: Gas Phase Reactions Recommended for Inclusion in the NASA Data Panel Report

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INTRODUCTION

The report, *Recommendations for Data Evaluation for Tropospheric Chemistry* [Herron, 1994], prepared for the NASA Panel for Data Evaluation, included the following set of recommendations:

1. Maintain and, as required, expand the current emphasis on heterogeneous chemistry as it applies to the troposphere. This is an active research area in which new phenomena can be expected to be discovered.

2. Initiate a new activity on aqueous chemical kinetics.

3. Extend the database to include the full tropospheric chemistry cycle through the C3 hydrocarbons, including their oxidation products and all possible nitrogen containing products.

4. For hydrocarbons larger than C3, develop empirical and/or theoretical methods for the direct estimation of the kinetics of reactions of the larger organic compounds in the atmosphere.

This section deals with recommendation number 3.

First, we outline the chemistry cycles involving the C1 to C3 hydrocarbons, including the nitrogen- and oxygen-containing products. These are the conventional "smog" chemistry reactions. Then, we tabulate the specific reactions of interest, including rate constants, if available. A final section deals with the chemistry of acetone, and some aspects of the chemistry of nitrogen containing products.

THE GENERAL MECHANISM FOR REACTION OF ORGANIC COMPOUNDS IN THE ATMOSPHERE OF SIGNIFICANCE TO SUBSONIC AIRCRAFT EMISSIONS

In general, organic compounds in the upper troposphere, the region of interest for subsonic emissions, will react exclusively with OH radicals to generate alkyl radicals. This will be the case for alkanes and alkenes. Alkynes may behave somewhat differently. The rate constants for most OH reactions are well known.

The subsequent fate of the alkyl radical is reaction with O_2 to yield an alkyl peroxy radical. It is the subsequent fate of these radicals, i.e., their reactions with NO, NO_2, OH, HO_2, other RO_2 radicals, etc., which is the subject of this report.

In particular, we are interested in the reactions of NO with RO_2 radicals which lead to the formation of RO radicals, which, depending on molecular complexity, can lead to new kinds of reactive species through reaction with O_2 or other radical species, or through bond scission or isomerization. Although not important for small organic substrates (less than C4), decomposition or isomerization could become increasingly important for larger species.

Generalized reaction mechanisms for upper tropospheric chemistry relevant to the subsonic aircraft emission problem are given in Figures 5.2-1, 5.2-2, and 5.2-3 for the alkanes, alkenes, and acetylene. The atmospheric chemistry of acetylene is in particularly poor shape, and Figure 5.2-3, and the tables of data which follow are little more than reaction lists.
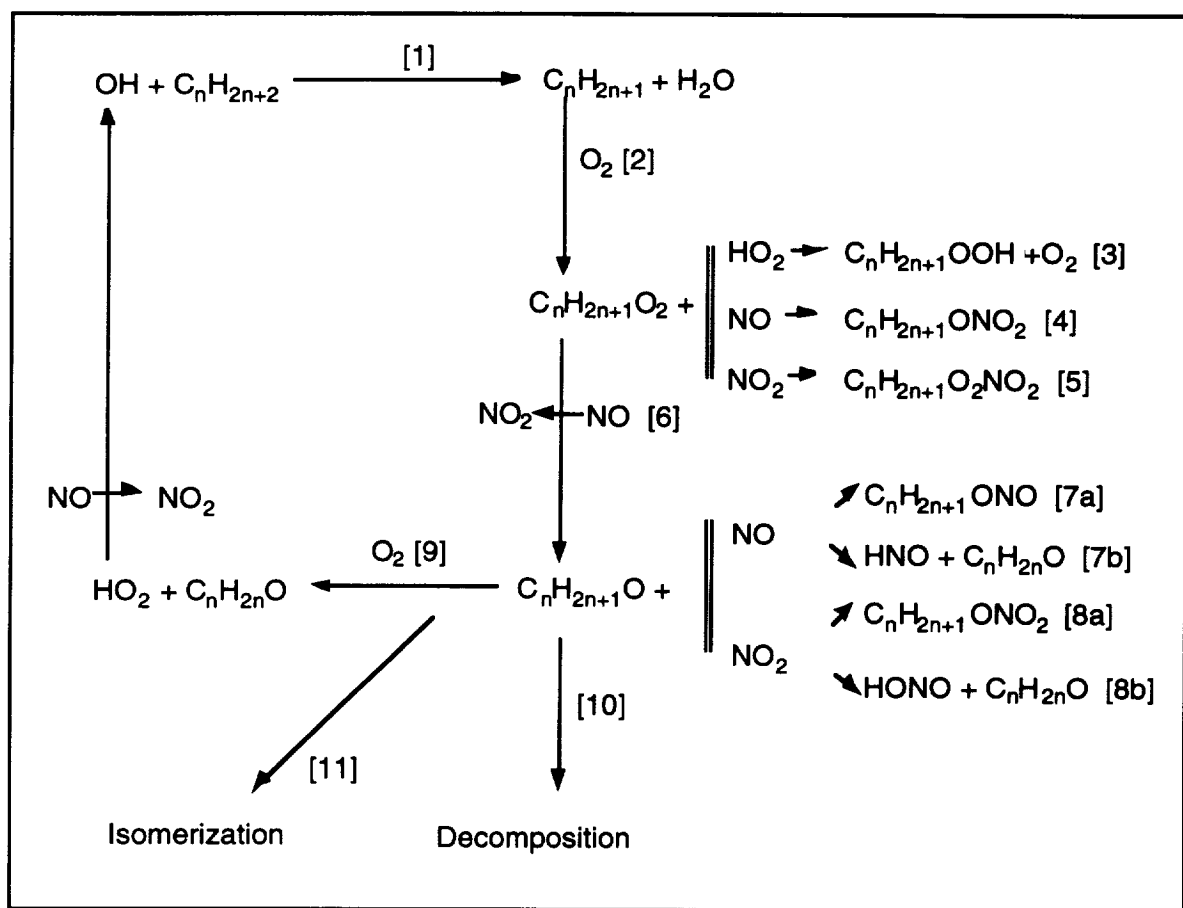
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Figure 5.2-1. Reaction paths for the alkanes.

[1]. Major path for alkane loss. For $\geq$ C3, different radical products depending on kind and number of C-H bonds.

[2]. Only reaction path for alkyl radicals. In fall-off for small radicals at 300 K at or below 1 bar.

[3].There are few data. Importance depends on the concentration of NO. Atkinson [1994] suggests using k (HO_2 + RO_2) = 3.5 x 10^{-13} exp(1000/T) cm^3 molecule^{-1} s^{-1}.

[4]. Could be important for $\geq$ C4 compounds. For small radicals (C1 and C2) not important. But for larger radicals, especially secondary radicals, could become significant. Using a method given in Atkinson [1990], can estimate this channel could account for 4% of the total reaction in the case of isopropoxy at room temperature.

[5] Strongly reversed at 300 K, 1 bar. May be more important at 200 K or less. Atkinson [1994] suggests k_{∞}^{300}=9 x 10^{-12} cm^3 molecule^{-1} s^{-1}, approximately temperature independent 250 to 350 K. In fall-off for C1 and C2 radicals at 300 K and 1 bar.

[6]. Always the major path for RO_2 loss. Atkinson [1994] suggests using k (NO + RO_2) = 4.9 x 10^{-12} exp(180/T) cm^3 molecule^{-1} s^{-1}. Note that this is the overall rate constant and will include contributions from [4].

[7]. Channel (a) is reversed by photolysis during the day. Channel (b) may be significant for $\geq$ C2 compounds (20%?)

[8]. Could be important for $\geq$ C4 compounds. Might be enhanced at lower temperatures. Channel (b) is negligible at 300 K, so probably will not be of any importance at lower temperatures.

[9]. Probably always the most important loss mechanism for small alkoxy radicals. This is not the case for hydroxy-substituted radicals, see notes to Figure 2.

[10]. Decomposition could be important for larger radicals ($\geq$ C4). However, the temperature dependence will make this kind of reaction much less important at higher altitudes and lower temperatures.

[11]. Although 1,4 and 1,5 H atom migration are possible for larger radicals, the reaction will be increasingly unimportant at lower temperatures.
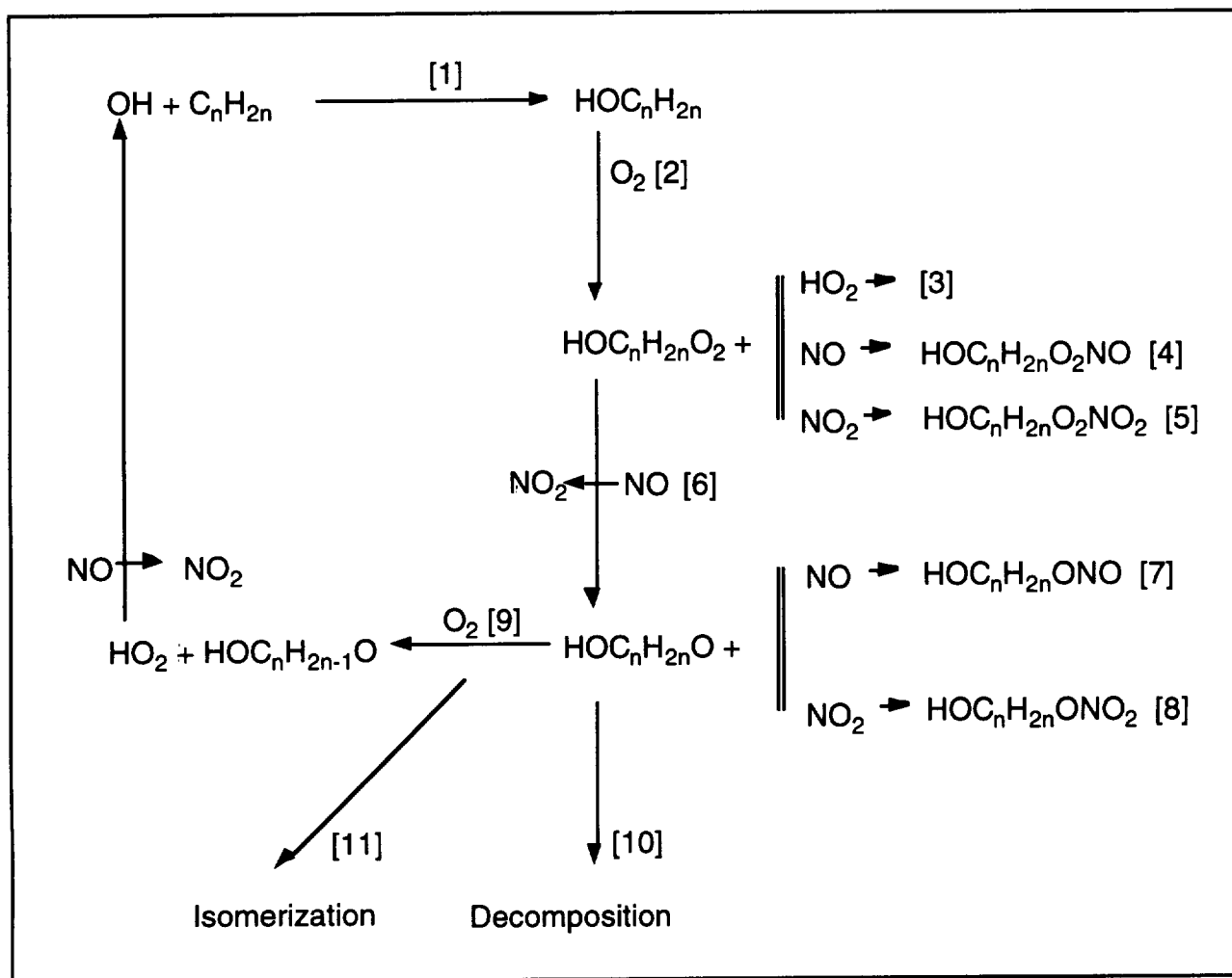
Figure 5.2-2. Reaction paths for the alkenes.

[1]. Assumed to be all addition. Abstraction channels may be of some importance at high temperatures for some alkenes. For non-symmetrical alkenes there are two possible sites of addition, with the least substituted being favored.

[2]. Only reaction path for hydroxyalkyl radicals.

[3-8]. Similar to alkane derived radical chemistry.

[9]. Significant only for C_2H_4. But could be more important at lower temperatures.

[10]. Major path. Products are α-hydroxy radicals and an aldehyde or ketone. The α-hydroxy radicals react further with O_2 to form HO_2 and another aldehyde or ketone. However, there is evidence that for $\geq C5$ 1-alkenes, paths including isomerization may become important [see Atkinson, 1994].

[11]. Unimportant for small radicals, but may be significant for larger ones.
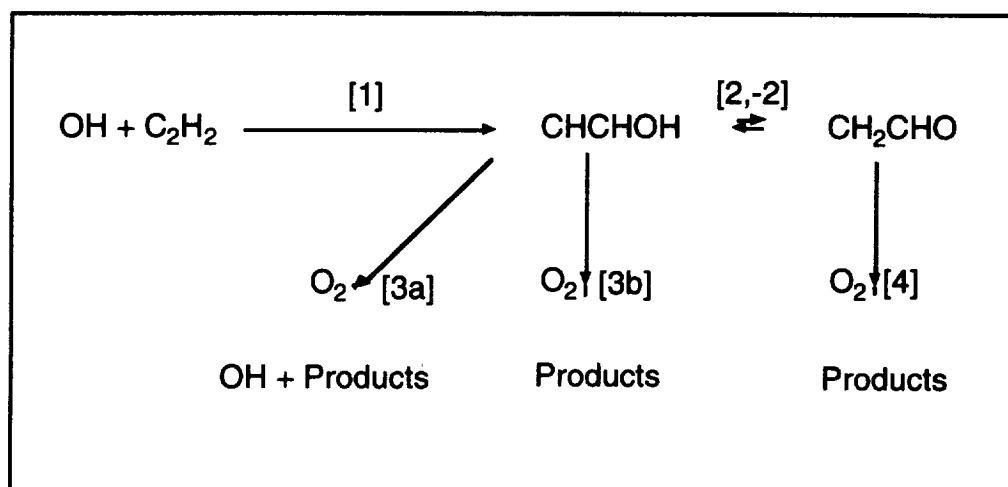
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Figure 5-2.3. Reaction path for acetylene[a].

a. Reactions of any adducts formed in reactions 3 or 4 with NO or other radical species are not included. See discussion in Atkinson [1990] and Siese and Zetzsch [1995].

[1]. Addition is probably the only channel. The back reaction is probably negligible. Decomposition of the unstabilized adduct to form CH_2CO + H is probably minor [see Siese and Zetzsch, 1995], but there are few data.

[2,4]. Vinoxy has been observed for C_2H_2, but the data suggest that this is a minor path.

[3]. The details are not known. The data indicate that [3a] is a major channel, regenerating OH [see Siese and Zetzsch, 1995].

One aspect of the atmospheric chemistry problem not addressed in detail here, is that relating to nighttime chemistry, i. e., reactions of the nitrate radical. For the small alkanes that is probably of no consequence. However, for larger alkanes or branched chain alkanes, as well as unsaturated hydrocarbons, the role of NO_3 may need to be considered. Some reactions are included in the tables.

ATMOSPHERIC CHEMISTRY OF THE C1-C3 HYDROCARBONS AND THEIR REACTION PRODUCTS

The reactions relevant to the subsonic chemistry problem are summarized in Tables 5.2-1 through 5.2-12 at the end of this section. Citations to NASA refer to the 1994 edition of the NASA tables [DeMore et al., 1994], while citations to IUPAC refer to the 1992 edition of that set of tables. Other citations are given by year and first three letters of the first authors name. All citations are given in the references. Since the data entries are not based on an exhaustive literature search, some data may have been overlooked.

¶ in the note column means that the reaction should be considered for inclusion in the NASA database. If the reaction is also shaded, it indicates a priority reaction for inclusion. If already in the NASA database, it is not further identified. A question mark in the note column means that the reaction could be important, but that there is insufficient data to make a decision.

Units are as follows:

First-order reactions: s^{-1}
Second-order reactions: cm^3 molecule^{-1} s^{-1}
Third-order reactions: cm^6 molecule^{-2} s^{-1}
E/R: K

SPECIAL TOPICS: ACETONE AND NITROGEN CONTAINING ORGANIC COMPOUNDS

Because of its ubiquitous nature in the troposphere, it seems worthwhile to include acetone in this report as the only oxygen containing organic compound.

The reaction paths are shown in Figure 5.2-4, by analogy with the corresponding alkane reactions. Photolysis is not included here, but must be included in the database for acetone. The temperature dependence of the absorption cross section has been measured, and the lifetime with respect to photolysis calculated at 220 K (10 km) to be 1.7×10^6 s, compared to the lifetime with respect to reaction with OH of 1.2×10^7 s [Hynes et al., 1992]. Thus, photolysis will be the major loss process during the day, leading to the formation of CH_3CO which then reacts further with O_2 to form CH_3COO_2 and PAN [see Singh et al., 1994]. Acetone is probably formed in the troposphere through oxidation of propane. Reactions of CH_3COO_2 and PAN related reactions are included in Tables 5.2-13 and 5.2-14 at the end of this section.

SUMMARY AND RECOMMENDATIONS

This report is essentially a list of reactions related to the tropospheric chemistry of the hydrocarbons through C3 and of acetone, that should be considered for inclusion in the NASA data evaluation. The tables list 97 reactions, many with no data entry. Of these, 52 should be considered by the panel, and 39 given highest priority for inclusion.

Extension of the database to larger organic compounds will be considered in a final report.
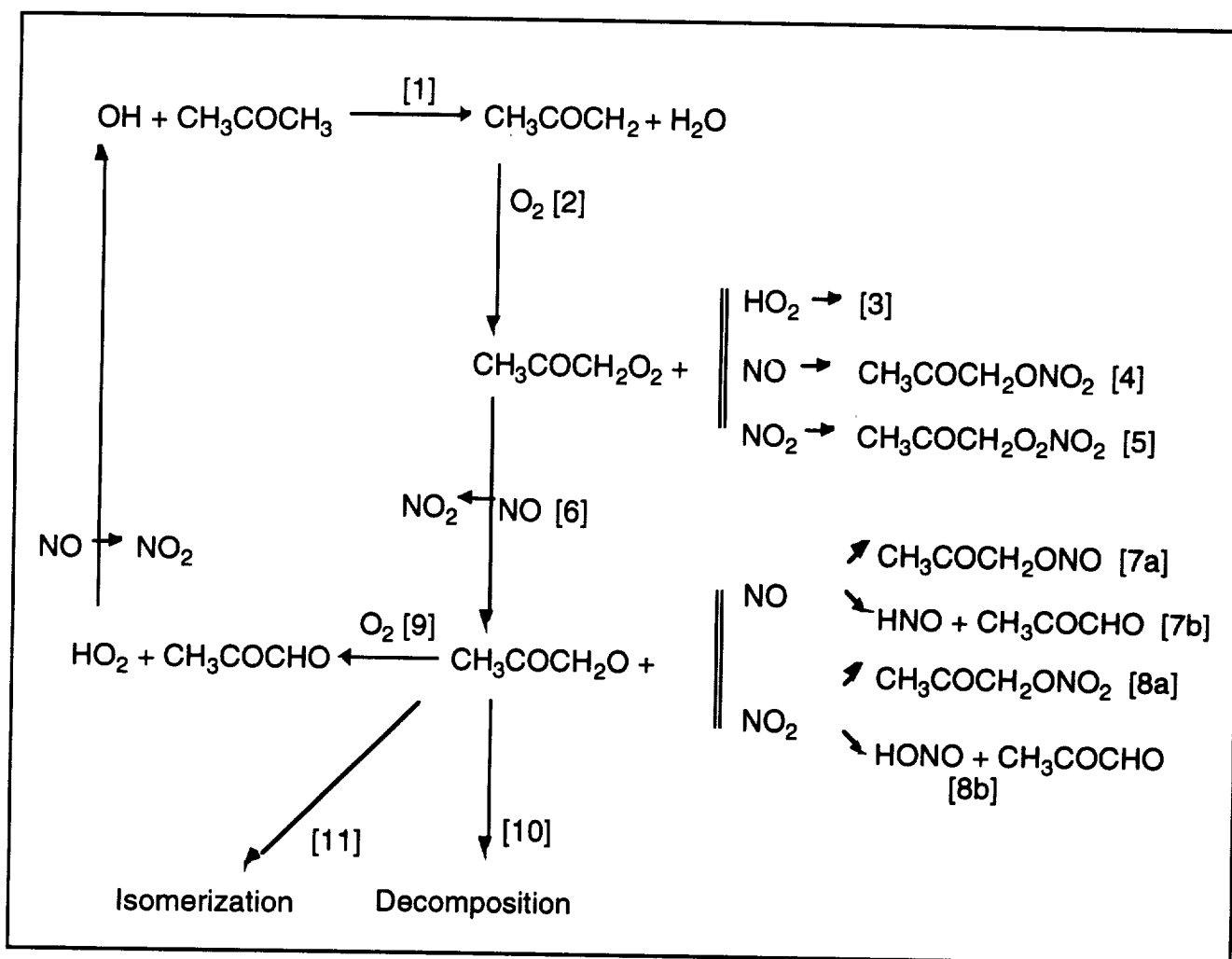
Figure 5-2.4. Reaction paths for acetone.

[1-8]. Comparable to alkane reactions of Figure 1.
[9]. Probably the major loss process for CH_3COCH_2O.
[10]. Probably unimportant. See Jenkins *et al.* [1993].
[11]. Probably unimportant.

Table 5.2-1. Reactions of CH_4. Rate constants for second-order reactions.

No	Reaction	A	E/R	k(298)	Source	Note
1.1	$CH_4 + OH \rightarrow CH_3 + H_2O$	2.65 (-12)	1800	6.3 (-15)	NASA	
		3.9 (-12)	1885	7.0 (-15)	IUPAC	
1.2	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	4.2 (-12)	-180	7.7 (-12)	NASA	
		4.2 (-12)	-180	7.6 (-12)	IUPAC	
1.3	$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$	3.8 (-13)	-800	5.6 (-12)	NASA	1
		3.8 (-13)	-780	5.2 (-12)	IUPAC	
1.4	$CH_3O + O_2 \rightarrow HCHO + HO_2$	3.9 (-14)	900	1.9 (-15)	NASA	
		7.2 (-14)	1080	1.9 (-15)	IUPAC	
1.5	$CH_3O + NO \rightarrow HCHO + HNO$			<8 (-12)	NASA	2
		4 (-12)	$(T/300)^{-0.7}$	4 (-12)	IUPAC	3
1.6	$CH_3O + NO_2 \rightarrow HCHO + HONO$				NASA	4
					IUPAC	5
1.7	$CH_4 + NO_3 \rightarrow CH_3 + HNO_3$			< (-18)	94ATK	

1. Products not specified.
2. Main channel addition. See Table 5.2-2. Depends on T and P. Reported value refers to "lower atmosphere."
3. Main channel at low pressure.
4. Main channel addition. See Table 5.2-2.
5. Main channel addition. See Table 5.2-2. A value was reported from the literature, but the reaction is unimportant at pressures greater than about 10 Torr.

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Table 5.2-2. Reactions of CH_4. Rate constants for three-body reactions.

No	Reaction	Low Pressure Limit $k_0(T)=k_0^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T)=k_\infty^{300}(T/300)^{-m}$		F_c	Source	Note
		k_0^{300}	n	k_∞^{300}	m			
2.1	$CH_3 + O_2 \rightarrow CH_3O_2$	4.5 (-31)	3.0	1.8 (-12)	1.7	0.6	NASA	
		1.0 (-30)	3.3	2.2 (-12)	-1.0	0.27	IUPAC	
2.2	$CH_3O_2 + NO_2 \rightarrow$ $CH_3O_2NO_2$	1.5 (-30)	4.0	6.5 (-12)	2.0	0.6	NASA	1
		2.5 (-30)	5.5	7.5 (-12)	0	0.4	IUPAC	
2.3	$CH_3O + NO \rightarrow$ CH_3ONO	1.4 (-29)	3.8	3.6 (-11)	0.6	0.6	NASA	
		1.6 (-29)	3.5	3.6 (-11)	0.6	0.6	IUPAC	
2.4	$CH_3O + NO_2 \rightarrow$ CH_3ONO_2	2.8 (-29)	4.0	2.0 (-11)	1.0	0.6	NASA	
		2.8 (-29)	4.5	2 (-11)	0	0.44	IUPAC	

1. Also reports the equilibrium constant.

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Table 5.2-3. Reactions of C_2H_6. Rate constants for second-order reactions.

No	Reaction	A	E/R	k(298)	Source	Note
3.1	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	8.7 (-12)	1070	2.4 (-13)	NASA	
		7.8 (-12)	1020	2.5 (-13)	IUPAC	
3.2	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	8.7 (-12)	0	8.7 (-12)	NASA	
				8.9 (-12)	IUPAC	
3.3	$C_2H_5O_2 + HO_2 \rightarrow C_2H_5O_2H + O_2$	7.5 (-13)	-700	8.0 (-12)	NASA	1
		6.5 (-13)	-650	5.8 (-12)	IUPAC	
3.4	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	6.3 (-14)	550	1.0 (-14)	NASA	1
		6.0 (-14)	550	9.5 (-15)	IUPAC	
3.5	$C_2H_5O + NO \rightarrow CH_3CHO + HNO$				NASA	2
				1.3 (-11)	IUPAC	2,3
3.6	$C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO$				NASA	2
					IUPAC	2,4
3.7	$C_2H_6 + NO_3 \rightarrow C_2H_5 + HNO_3$			1.4 (-18)	94ATK	¶ 3

1. Products not specified.
2. See Table 5.2-4.
3. Estimated.
4. Minor channel.

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Table 5.2-4. Reactions of C_2H_6. Rate constants for three-body reactions.

No	Reaction	Low Pressure Limit $k_0(T)=k_0^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T)=k_\infty^{300}(T/300)^{-m}$		F_c	Source	Note
		k_0^{300}	n	k_∞^{300}	m			
4.1	$C_2H_5 + O_2 \rightarrow C_2H_5O_2$	1.5 (-28)	3.0	8.0 (-12)	0	0.6	NASA	
		5.9 (-29)	3.8	7.8 (-12)	0	0.54	IUPAC	
4.2	$C_2H_5O_2 + NO \rightarrow C_2H_5ONO_2$			≤1.3 (-13)			IUPAC	1
4.3	▓▓▓▓▓▓	1.3 (-29)	6.2	8.8 (-12)	0	0.31	IUPAC	¶
4.4	$C_2H_5O + NO \rightarrow C_2H_5ONO$	2.0 (-27)	4.0	4.4 (-11)	1.0	0.6	NASA	
				4.4 (-11)	0		IUPAC	
4.5	$C_2H_5O + NO_2 \rightarrow C_2H_5ONO_2$	2.0 (-27)	4.0	2.8 (-11)	1.0	0.6	NASA	
				2.8 (-11)	0		IUPAC	

1. At 1 bar.

Table 5.2-5. Reactions of C_3H_8. Rate constants for second-order reactions.

No	Reaction	A	E/R	k(298)	Source	Note
5.1	$C_3H_8 + OH \rightarrow C_3H_7 + H_2O$	1.0 (-11)	660	1.1 (-12)	NASA	1
		9.8 (-12)	640	1.14 (-12)	IUPAC	1
5.2				8.7 (-12)	IUPAC	¶
5.3				8.5 (-12)	IUPAC	¶
5.4				8 (-15)	IUPAC	¶
5.5		1.5 (-14)	200	8 (-15)	IUPAC	¶
5.6	$n\text{-}C_3H_7O + NO \rightarrow C_2H_5CHO + HNO$					?
5.7	$l\text{-}C_3H_7O + NO \rightarrow CH_3COCH_3 + HNO$			6-5 (-12)	IUPAC	?
5.8	$n\text{-}C_3H_7O + NO_2 \rightarrow C_2H_5CHO + HONO$					?
5.9	$l\text{-}C_3H_7O + NO_2 \rightarrow CH_3COCH_3 + HONO$					?
5.10	$C_3H_8 + NO_3 \rightarrow C_3H_7 + HNO_3$			1.7 (-17)	94ATK	¶ 1,2

1. Total rate constant.
2. Estimate.

Table 5.2-6. Reactions of C_3H_8. Rate constants for three-body reactions.

No	Reaction	Low Pressure Limit $k_0(T)=k_0^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T)=k_\infty^{300}(T/300)^{-m}$		F_c	Source	Note
		k_0^{300}	n	k_∞^{300}	m			
6.1				8 (-12)	0		IUPAC	¶
6.2				1.1 (-11)	0		IUPAC	¶
6.3				1.8 (-13)			IUPAC	¶ 1
6.4				3.7 (-13)			IUPAC	¶ 1
6.5				8 (-12)			90ATK	¶ 2
6.6				8 (-12)			90ATK	¶ 2
6.7								¶
6.8				3.4 (-11)	0		IUPAC	¶
6.9								¶
6.10				3.5 (-11)	0		IUPAC	¶

1. At 1 bar.
2. Estimate. Approximately temperature independent.

Table 5.2-7. Reactions of C_2H_4. Rate constants for second-order reactions.

No	Reaction	A	E/R	k(298)	Source	Note
7.1	HOCH$_2$CH$_2$O$_2$ + NO → HOCH$_2$CH$_2$O + NO$_2$			9.0 (-12)	94ATK	¶ 1
7.2	HOCH$_2$CH$_2$O$_2$ + HO$_2$ → Products			1 (-11)	IUPAC	¶ 2
7.3	HOCH$_2$CH$_2$O + O$_2$ → HOCH$_2$CHO + HO$_2$					¶
7.4	HOCH$_2$CH$_2$O + NO → HOCH$_2$CHO + HNO					
7.5	HOCH$_2$CH$_2$O + NO$_2$ → HOCH$_2$CHO + HONO					
7.6	CH$_2$OH + O$_2$ → HCHO + HO$_2$			9.1 (-12)	NASA	
				9.4 (-12)	IUPAC	
7.7	CH$_2$CH$_2$ + NO$_3$ → Products	3.3 (-12)	2880	2.1 (-16)	IUPAC	¶ 3

1. Estimate from Becker [1991].
2. Taken as identical to C$_2$ H$_5$O$_2$ + HO$_2$.
3. Probably an addition reaction. No data on pressure dependence, but epoxides are found as major products at lower pressures for larger alkenes.

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Table 5.2-8. Reactions of C_2H_4. Rate constants for three-body reactions.

No	Reaction	Low Pressure Limit $k_0(T)=k_0^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T)=k_\infty^{300}(T/300)^{-m}$		F_c	Source	Note
		k_0^{300}	n	k_∞^{300}	m			
8.1	CH_2CH_2 + OH → $HOCH_2CH_2$	1.0 (-28)	0.80	8.8 (-12)	0	0.6	NASA	1
		7 (-29)	3.1	9 (-12)	0	0.7	IUPAC	
8.2	▓▓▓▓▓▓			3 (-12)			IUPAC	¶ 2
8.3	$HOCH_2CH_2O_2$ + NO → $HOCH_2CH_2ONO_2$							¶
8.4	$HOCH_2CH_2O_2$ + NO_2 → $HOCH_2CH_2O_2NO_2$							¶
8.5	▓▓▓▓▓▓							¶
8.6	▓▓▓▓▓▓							¶
8.7	▓▓▓▓▓▓							¶

1. Could be a small activation barrier.
2. Products not specified. Close to or at high pressure limit.

Table 5.2-9. Reactions of C_3H_6. Rate constants for second-order reactions[a].

No	Reaction	A	E/R	k(298)	Source	Note
9.1	$HOCH_2CH(O_2)CH_3 + NO \rightarrow$ $HOCH_2CH(O)CH_3 + NO_2$					¶
9.2	$HOCH_2CH(O_2)CH_3 + HO_2 \rightarrow$ Products					
9.3	$HOCH_2CH(O)CH_3 + O_2 \rightarrow HOCH_2COCH_3$ $+ HO_2$					¶
9.4	$HOCH_2CH(O)CH_3 + NO \rightarrow HOCH_2COCH_3$ $+ HNO$					
9.5	$HOCH_2CH(O)CH_3 + NO_2 \rightarrow$ $HOCH_2COCH_3 + HONO$					
9.6	$HOCHCH_3 + O_2 \rightarrow CH_3CHO + HO_2$					¶
9.7	$CH_2CHCH_3 + NO_3 \rightarrow$ Products			9.4 (-15)	IUPAC	¶ 1
		4.6 (-13)	1156	9.5 (-15)	94ATK	

a. Reactions are shown only for the terminal OH addition sequence which accounts for about 66% of the total reaction at 300 K. Reaction 9.6 is an exception, $HOCHCH_3$ being a product of non-terminal addition.

1. Probably an addition reaction. No data on pressure dependence, but epoxides are found as major products at lower pressures for larger alkenes.

Table 5.2-10. Reactions of C_3H_6. Rate constants for three-body reactions[a].

No	Reaction	Low Pressure Limit $k_0(T)=k_0^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T)=k_\infty^{300}(T/300)^{-m}$		F_c	Source	Note
		k_0^{300}	n	k_∞^{300}	m			
10.1	CH_2CHCH_3 + OH → $HOCH_2CHCH_3$	8 (-27)	3.5	3.0 (-11)	0	0.5	IUPAC	¶
10.2								¶
10.3	$HOCH_2CH(O_2)CH_3$ + NO → $HOCH_2CH(ONO_2)CH_3$							¶
10.4	$HOCH_2CH(O_2)CH_3$ + NO_2 → $HOCH_2CH(O_2NO_2)CH_3$							¶
10.5								¶
10.6								¶
10.7								¶
10.8								¶

a. Reactions are shown only for the terminal OH addition sequence which accounts for about 66% of the total reaction at 300 K. Reaction 10.8 is an exception, $CH_3CH(OH)CH_2O$ being a product of non-terminal addition.

Table 5.2-11. Reactions of C_2H_2. Rate constants for second-order reactions.

No	Reaction	A	E/R	k(298)	Source	Note
11.1	$HOC_2H_2 + O_2 \rightarrow OH + Products$			4.2 (-12)	95SIE	¶ 1
11.2	$HOC_2H_2O_2 + NO \rightarrow NO_2 + HOC_2H_2O$					?
11.3	$C_2H_2 + NO_3 \rightarrow Products$			<1 (-16)	IUPAC	¶ 2
		4.9 (-13)	2740	5 (-17)	88CAN	

1. Small negative temperature coefficient? Although given as a second order reaction, it presumably involves an adduct. Near room temperature, the adduct may have a very short lifetime with respect to formation of OH. However, there are no data as regards lifetime at low temperature.
2. Probably an addition reaction. No data on pressure dependence.

Table 5.2-12. Reactions of C_2H_2. Rate constants for three-body reactions.

No	Reaction	Low Pressure Limit $k_0(T)=k_0^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T)=k_\infty^{300}(T/300)^{-m}$		F_c	Source	Note
		k_0^{300}	n	k_∞^{300}	m			
12.1	$C_2H_2 + OH \rightarrow HOC_2H_2$	5.5 (-30)	0	8.3 (-13)	-2	0.6	NASA	1
		5 (-30)	1.5	9.0 (-13)	-2	0.62	IUPAC	1
12.2	$HOC_2H_2O_2 + NO \rightarrow HOC_2H_2ONO_2$							?
12.3	$HOC_2H_2O_2 + NO_2 \rightarrow HOC_2H_2O_2NO_2$							?
12.4	$HOC_2H_2O + NO \rightarrow HOC_2H_2ONO$							?
12.5	$HOC_2H_2O + NO_2 \rightarrow HOC_2H_2ONO_2$							?

1. Negative value for m based on a 5 kJ mol⁻¹ barrier for addition.

Table 5.2-13. Reactions of CH_3COCH_3. Rate constants for second-order reactions.

No	Reaction	A	E/R	k(298)	Source	Note
13.1	CH₃COCH₂ + OH → CH₃COCH₂ + H₂O	1.7 (-12)	600	2.3 (-13)	IUPAC	¶
13.2	CH₃COCH₂O₂ + NO → CH₃COCH₂O + NO₂					¶
13.3	$CH_3COCH_2O_2$ + HO_2 → CH_3COCH_2OOH + O_2					
13.4	CH_3COCH_2O + O_2 → CH_3COCHO + HO_2					¶
13.5	CH_3COCH_2O + NO → CH_3COCHO + HNO					
13.6	CH_3COCH_2O + NO_2 → CH_3COCHO + HONO					
13.7	CH_3COCH_3 + NO_3 → CH_3COCH_2 + HNO_3			≤1 (-17)	94ATK	¶ 1
13.8	CH_3COO_2 + NO → CH_3 + CO_2 + NO_2	2.4 (-11)	0	2.4 (-11)	NASA	2
		2.0 (-11)	0	2.0 (-11)	IUPAC	
13.9	$CH_3COO_2NO_2$ + OH → Products			<4 (-14)	NASA	3
		9.5 (-13)	650	1 (-13)	IUPAC	

1. From Boyd *et al.* [1991].
2. Products not specified in Demore *et al.* [1994]. Suggest $CH_3C(O)O$ + NO_2.
3. Probable products HO_2 + $CH_2 COO_2 NO_2$.

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Table 5.2-14. Reactions of CH_3COCH_3. Rate constants for three-body reactions.

	Reaction	Low Pressure Limit $k_0(T)=k_0^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T)=k_\infty^{300}(T/300)^{-m}$		F_c	Source	Note
		k_0^{300}	n	k_∞^{300}	m			
14.1	$CH_3COCH_2 + O_2 \rightarrow$ $CH_3COCH_2O_2$			1.5 (-12)			IUPAC	¶ 1
14.2	$CH_3COCH_2O_2 + NO \rightarrow$ $CH_3COCH_2ONO_2$							¶
14.3	$CH_3COCH_2O_2 + NO_2 \rightarrow$ $CH_3COCH_2O_2NO_2$							¶
14.4	$CH_3COCH_2O + NO \rightarrow$ CH_3COCH_2ONO							¶
14.5	$CH_3COCH_2O + NO_2 \rightarrow$ $CH_3COCH_2ONO_2$							¶
14.6	$CH_3COO_2 + NO_2 \rightarrow$ $CH_3COO_2NO_2$	9.7 (-29)	5.6	9.3 (-12)	1.5	0.6	NASA	
		2.7 (-28)	7.1	1.2 (-11)	0.9	0.3	IUPAC	
14.7	$CH_3COO_2NO_2 \rightarrow$ $CH_3COO_2 + NO_2$						IUPAC	¶ 2, 3

1. From Cox *et al.* [1990]. Close to or at the high pressure limit.
2. Reported in Atkinson *et al.* [1992] as $k_0 = 4.9 \times 10^{-3} \exp(-12100/T)$ s^{-1}, $k_\infty = 4.0 \times 10^{16} \exp(-13600/T)$ s^{-1}, $F_c= 0.3$. Based on essentially same data as for the reverse reaction, 14.6.
3. Explicitly, or as the equilibrium constant.

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Section 5.3

Recommendations for Data Evaluation for Tropospheric Chemistry: Methods for Estimating Rate Constants and Some Concluding Remarks

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INTRODUCTION

The report, *Recommendations for Data Evaluation for Tropospheric Chemistry* [Herron, 1994], prepared for the NASA Panel for Data Evaluation, included the following set of recommendations:

1. Maintain, and as required, expand the current emphasis on heterogeneous chemistry as it applies to the troposphere. This is an active research area in which new phenomena can be expected to be discovered.

2. Initiate a new activity on aqueous chemical kinetics.

3. Extend the database to include the full tropospheric chemistry cycle through the C3 hydrocarbons, including their oxidation products and all possible nitrogen containing products.

4. For hydrocarbons larger than C3, develop empirical and/or theoretical methods for the direct estimation of the kinetics of reactions of the larger organic compounds in the atmosphere.

Recommendation number 3 was considered in Section 5.2. This section deals with recommendation number 4.

An outline of the cycles of chemistry involving the C1 to C3 hydrocarbons and of acetone, including the nitrogen and oxygen containing products, was given earlier [Herron, 1995], and will not be repeated here. We also gave a tabulation of readily available data for reactions judged important to the subsonic aircraft chemistry problem. These are the basis for seeking out estimation methods which would allow us to extend the database to larger organic compounds.

CLASSES OF REACTION OF ORGANIC COMPOUNDS IN THE ATMOSPHERE OF SIGNIFICANCE TO SUBSONIC AIRCRAFT EMISSIONS

In general, organic compounds in the upper troposphere, the region of interest for subsonic emissions, will react exclusively with OH radicals (or possibly with NO_3 radicals at night) to generate alkyl radicals. This will be the case for alkanes and alkenes. Alkynes may behave somewhat differently. The possible role of ozone reactions with a very limited number of organic compounds is recognized but not considered further and we do not include estimation methods here.

The fate of the alkyl radical is reaction with O_2 to yield the alkyl peroxy radical. It is the subsequent fate of these radicals, i.e., their reactions with NO, NO_2, OH, HO_2, other RO_2 radicals, etc., which is of greatest interest with respect to subsonic aircraft. In particular, we are interested in the reactions of NO with RO_2 radicals which lead to the formation of RO radicals which, depending on molecular complexity, can lead to new kinds of reactive species through reaction with O_2 or other radical species, or through decomposition or isomerization. Although less important for small organic substrates (less than C4), decomposition or isomerization will become increasingly important for larger species, and this will be one of the major focus areas for considering estimation methods.

ESTIMATION METHODS

Estimation methods for larger organic compounds have been developed for use in combustion chemistry or for application to the lower troposphere. In the case of the latter, this means

temperatures close to 298 K, and pressures close to 1 bar. Many of these approaches are discussed by Atkinson [1994], and that work is the basis of this report. For the subsonic aircraft chemistry problem, we need kinetics data valid over the temperature range of about 200 to 300 K, and a pressure range of about 0.1 to 1 bar.

We need this data for two kinds of processes: abstraction reactions, involving removal of an H atom, and unimolecular/association reactions. In theory, we can calculate rate constants using estimation methods, or a range of more rigorous theoretical methods. The approach is dictated by the accuracy requirements of the model. In practice, we are severely limited; there are only a few approaches to abstraction reactions, and even fewer ways of approaching unimolecular reactions.

What is astonishing in considering this problem is the marginal progress made since the last (and only serious) effort made to address the data problems of tropospheric kinetics in 1979 [Herron et al., 1979]. If we exclude data on OH kinetics, the database for organics beyond even C2 is hardly much larger today that it was then. This makes the validation of any kind of non-experimental method hard, if not impossible, to achieve.

As noted earlier, the effect of temperature on rate constants is crucial in determining the nature of the final products. This is illustrated in Table 5.3-1, where we calculate rate constants for selected reactions at different temperatures, using data from DeMore et al. [1994] or Atkinson et al. [1992], or estimated using some of the methods discussed below. In some cases the data are extrapolated well outside the range of validity. These values are for illustration only, and not for use in modeling calculations. However, they indicate not only the crucial importance of temperature in modeling the range of kinetics that is encountered in the troposphere, but also the problems that can be expected in estimating rate constants at lower temperatures.

ABSTRACTION REACTIONS

OH

Group methods for OH abstraction reactions are well established [Atkinson, 1987; Kwok and Atkinson, 1995], and we probably have good group terms for all possible reactions of interest

Table 5.3-1. Rate Constants at 300 K and 250 K for Some Tropospheric Reactions[a].

	$R=CH_3CH_2$		$R=CH_3CHCH_2CH_3$		$R=CH_3CHCH_2CH_2CH_3$		$R=HOCH_2CH_2$	
	300 K	250 K	300 K	250 K	300 K	250 K	300 K	250 K
RO + O2 → HO2 + P	1.0 (-14)	7.0 (-15)	1.7 (-14)	1.5 (-14)	9.2 (-15)	7.8 (-15)	6.2 (-15)	5 (-15)
RO + NO → RONO	4.4 (-11)	5.3 (-11)	4.4 (-11)	5.3 (-11)				
RO + NO2 → RONO2	2.8 (-11)	3.4 (-11)	2.8 (-11)	3.4 (-11)				
RO → Products (decomposition)	1.5 (-1)	1.8 (-4)	5.4 (4)	8.6 (2)	4.9 (3)	40	8.6 (4)	1.2 (3)
RO → Products (isomerization)	-	-	-	-	6.7 (4)	4.5 (3)	-	-
k(RO + O2)/k(RO → Products)	3.3 (5)	2.3(7)	1.6	11	0.6	1.0	0.4	2.5

a. At the high pressure limit. Total pressure taken as 1 bar at 300 K and 0.1 bar at 250 K. Data derived from DeMore et al. [1994] and Atkinson et al. [1992] (as listed in Herron [1995]), or estimated using data in Atkinson [1994].

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here. Terms for calculating temperature dependence are also provided. Since most experimental data is centered around room temperature, it is difficult to know exactly how valid the derived numbers are at low temperature; probably good enough for modeling purposes.

Cohen [1990, 1991] has applied transition state theory to the calculation of rate constants for OH abstraction reactions. His approach is more rigorous than the group approach, and indicates that extension of group methods to larger chain compounds is not straightforward. Molecular size becomes an important factor leading to underprediction of the rate constants using conventional group methods.

However, it is doubtful that data will be needed for very large molecules, so this is probably not a major problem. In any case, the correction factors are not that large, and the predicted values using either the conventional groups or transition state calculations are within the uncertainty of the experimental data.

Group methods are also applicable to addition reactions [Atkinson, 1987; Kwok and Atkinson, 1995], but that is not treated here.

NO_3

Most of the available experimental data were taken at or above room temperature [Atkinson, 1991, 1994]. The Arrhenius plots become increasingly non-linear at the higher temperatures. The A factors are normal, with activation energies in the 6 kcal region. Extrapolation of the data to low temperatures will be highly uncertain (the rate constants at 250 K in Table 1 were obtained in this way, and are very unreliable). Group methods have been developed to predict rate constants at 298 K for primary, secondary and tertiary H atom abstraction [Atkinson 1991, 1994], but no temperature dependence has been derived. The group method was developed by correlating OH and NO_3 rate constants at room temperature. If a larger body of experimental data existed, it would be possible to extend the correlation to a wider temperature range. Alternatively, application of transition state theory might be a useful approach.

Since the activation energies for OH reactions are much smaller than for the corresponding NO_3 reactions, the latter will become much slower relatively at lower temperatures. For example, for n-butane at 298 K, k(OH) = 2.5 x 10^{-12} and k(NO_3) = 4.6 x 10^{-17}, whereas at 250 K, k(OH) = 2.0 x 10^{-12} and k(NO_3) = 5.6 x 10^{-18} all in cm^3 molecule^{-1} s^{-1}, favoring the OH reactions by a factor of about 10 in going from 298 to 250 K.

However, the estimated low temperature rate constants for the NO_3 reactions are very uncertain, and the role of nighttime chemistry has not been considered. Therefore, these reactions cannot be dismissed.

$RO + O_2 \rightarrow HO_2 + R'$
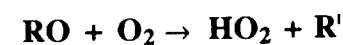
There are data for CH_3O, C_2H_5O, and $(CH_3)_2CHO$. On the basis of the data for C_2H_5O and $(CH_3)_2CHO$, Atkinson [1994] recommends:

k(primary alkoxy) = 6.0 x $10^{-14}e^{-550/T}$ cm^3 molecule^{-1} s^{-1}
k(secondary alkoxy) = 1.5 x $10^{-14}e^{-200/T}$ cm^3 molecule^{-1} s^{-1}

The experimental data were taken at T≥ 300 K, so their validity at lower temperatures is less certain. The A factors appear to be low, and non-Arrhenius behavior is exhibited in studies over wide temperature ranges for CH_3O.

Atkinson [1994] also gives a method based on reaction exothermicity (see his citations 56, 62, 63): $k = 1.3 \times 10^{-19} n e^{-(0.32\Delta H)}$ cm^3 molecule^{-1} s^{-1}, where n is the number of abstractable H atoms, and ΔH is the reaction exothermicity in kcal mol^{-1}. This is based on the three sets of kinetics data indicated above. It provides no information on temperature dependence, but in the absence of other data, the assumption that the reaction is temperature independent is reasonable. Atkinson [1994] provides tables of rate constants derived from these considerations which can be used as a check on calculations. Unfortunately, the thermochemical data base used in the calculations was not included. Radical enthalpies are the key quantities, some are listed in Atkinson and Carter [1991] but these quantities do seem to wander.

UNIMOLECULAR/ASSOCIATION REACTIONS

Aside from purely empirical approaches, these classes of reactions should be treated with some form of RRKM theory. The standard treatment is now some formulation of the Troe approach. Patrick and Golden [1983] treated a whole series of atmospherically important reactions in this manner, and this is presumably the basis for the treatment in the DeMore et al. [1994] evaluation, where the correction factor, F_c, is set at 0.6 and other parameters adjusted; in Atkinson et al. [1992], F_c, is calculated case by case. The end results are much the same. However, this approach implies that some data exist. In the absence of real data, these methods are not very practical.

RO + NO → RONO

Atkinson [1994] recommends $k_\infty = 2.3 \times 10^{-11} \exp(150/T)$ cm^3 molecule^{-1} s^{-1}. For larger radicals, these reactions are close to or at the high pressure limit at 298 K and 1 bar. This is probably also the case for all regions of the troposphere. There is a second path leading to HNO, but this is almost certainly unimportant under atmospheric conditions.

RO + NO$_2$ → RONO$_2$

The kinetics are similar to those for the corresponding NO reactions. Atkinson [1994] recommends $k_\infty = 2.3 \times 10^{-11} \exp(150/T)$ cm^3 molecule^{-1} s^{-1}.

RO → Products (Decomposition)

This is discussed in detail in Atkinson and Carter [1991]. Looking at the data given there, it is clear that E_a is closely related to the heat of reaction. Thus, exothermic reactions are all fast, and can be expected to be dominant with respect to reaction of RO with O_2. Endothermic reactions with large heats of reaction will be slow and reactions with intermediate heats of reaction will be competitive with the reaction of RO with O_2. Our ability to predict is constrained by the limitations of the thermodynamic data for the radicals.

Atkinson and Carter [1991], derived an expression based on reaction enthalpy for comparing the reactions RO → Products and RO + O_2 at 298 K. Atkinson [1994], using the same kind of data, gives an expression to estimate the rate constant for the decomposition channel at 298 K of $k = 2.4 \times 10^{17} nd \exp\{0.60\Delta H(RO + O_2)-1.33\Delta H(RO \to Products)\}$ s^{-1}, where n is the number of

abstractable H atoms, and d, the degeneracy of the decomposition reaction. To estimate the effect of temperature, it is suggested that this expression be used to derive k at 298 K, and k at other temperatures be calculated using a pre-exponential factor, $A_d = 2d \times 10^{14}$ s^{-1}.

These expressions have some use in estimating the relative importance of the different possible reactions for RO, but are based on a limited set of data of uncertain reliability.

Predicting rate constants based on uncertain thermochemical data is highly risky. An uncertainty in activation energy of 2 kcal mol^{-1} translates to an uncertainty in rate constant of about 30 at 300 K and 150 at 200 K.

RO → Products (Isomerization)

In most cases we assume that isomerization is unimportant compared to decomposition or reaction with O_2. However, there may be exceptions, particularly for large radicals for which isomerization could be competitive. Atkinson [1994] gives Arrhenius parameters for some 1,5-H shift reactions (six member cyclic transition states with estimated strain energies of 0.5 kcal mol^{-1}) estimated on the basis of RO abstraction rate constants adjusted for ring strain energy [see also Golden 1979]. As shown in Table 5.3-1, isomerization is predicted to be important for the $CH_3CH(O)CH_2CH_2CH_3$ radical at 298 K and 1 bar, and at 250 K and 0.1 bar.

There are no experimental data available to validate this approach to estimation (but isomeric products have been identified in some cases), and one expects the low temperature rate constants to be highly uncertain because of the uncertainty in estimated activation energy, as noted in the discussion of RO → Products (decomposition) above.

RO_2 + NO → $RONO_2$ (RO + NO_2)

These reactions are fast. For small radicals the only important channel is that leading to RO + NO_2. However, for larger radicals formation of the nitrate becomes more important. The reactions are complex, and although the overall rate constants are pressure independent, the branching ratios to yield either the nitrate or the products RO + NO_2 are pressure and temperature dependent. Although the experimental data are all taken near 300 K, the reaction is close to being temperature independent. Atkinson [1994] suggests $k = 4.9 \times 10^{-12}e^{180/T}$ cm^3 molecule^{-1} s^{-1}.

To obtain the branching ratio, Atkinson [1994] gives an expression for calculating the ratio k(RO_2 + NO →$RONO_2$)/k(RO_2 + NO → RO + NO_2) for secondary radicals as a function of temperature and pressure. These expressions are valid only for alkyl peroxy radicals. For primary and tertiary radicals, a correction factor is given, although it is not clear if this is valid only at room temperature.

Applying the recommended expressions to the radical $CH_3CH(OO)CH_2CH_2CH_3$, we estimate that k(RO_2 + NO → $RONO_2$)/k(RO_2 + NO →RO + NO_2) is 0.15 at 298 K, 1 bar, and 0.05 at 250 K, 0.1 bar. This indicates that formation of the nitrate will be less important in the upper troposphere.

There are no corresponding data for hydroxy substituted alkyl radicals. The rate constant ratios are probably lower, but there is no basis for estimation.

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$RO_2 + NO_2 \rightarrow RO_2NO_2$
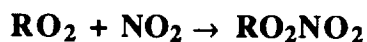
These reactions are fast, and probably at the high-pressure limit under tropospheric conditions. k_∞ is essentially temperature independent. Calculations using the DeMore et al. [1994] recommendations for $CH_3C(O)OO$ radicals or the Atkinson et al. [1992] recommendations for CH_3CH_2OO radicals at 298 K, 1 bar or 250 K, 0.1 bar, indicate marginal effects of pressure or temperature. Therefor, using the expression recommended by Atkinson [1994], $k = 9 \times 10^{-12}$ cm³ molecule^{-1} s^{-1}, will be valid for all the radicals larger than C2.

SOME FINAL REMARKS

The original recommendations for extension of the NASA database, to allow for including chemistry which might impact ozone or climate as a consequence of subsonic aircraft emissions, called for including more tropospheric chemistry.

One recommendation was to expand the database to include the C3 hydrocarbons (and acetone). In light of the paucity of experimental data even for these compounds, and the unlikely prospect of new measurements, the question of extension to larger molecules becomes of necessity a question of how the numbers can be obtained by estimation or calculation using higher levels of theory. At this time, the prospect of deriving data by either approach is dim.

The problem is compounded by the fact that it is not clear what kinds of data will be needed by the modeling community. What molecules will go into the models? What is the range of temperature and pressure over which the data are needed? Without the answers to these questions, worrying about predictive methods, beyond the simplest estimation or correlation methods, is indeed putting that proverbial vehicle before its means of locomotion.

What might be useful would be application of approaches such as the Melius BAC-MP4 method to some of these reactions. In particular, application to complex reactions with multiple product channels would be helpful. These approaches have been used in modeling combustion and propellent chemistry.

In comments on the second report in this series, Charles Kolb pointed out that many of the partial oxidation products, which will be formed in the atmospheric degradation of small organic compounds, will be soluble in aqueous droplets, and thus, we will need additional data on accommodation coefficients and other relevant quantities. Some, but by no means all information can be found in the most recent DeMore et al. [1994] data evaluation, and in the upcoming revision of the Atkinson et al. [1992] data evaluation.

Properties of the aqueous phase will also become increasingly important. Thus, aqueous kinetics was suggested as a new area of interest. The new activity that has been initiated within IUPAC on tropospheric aqueous kinetics should help to support that activity. Robert Huie of NIST and Peter Warneck of the Max-Plank Institute for Chemistry, Mainz, will be responsible for that project.

Table 5.3-2. Status of estimation methods for tropospheric chemistry.

Reaction Type	Database	Status of Estimation Method	Comments	Sources
$OH + ORG \rightarrow H_2O + P$	Very large	Good	Group method. T dependence less reliable at lower temperatures.	Atkinson[1987]; Kwok and Atkinson [1995]
$NO_3 + ORG \rightarrow HNO_3 + P$	Small	Poor	Group method. 298 K only.	Atkinson [1991]
$RO + O_2 \rightarrow HO_2 + P$	Small	Poor	T dependence small. Low temperature data uncertain.	Atkinson [1994]
$RO + NO \rightarrow RONO$	Small	Fair	Suitable to task. T dependence small.	Atkinson [1994]
$RO + NO_2 \rightarrow RONO_2$	Very small	Fair	Suitable to task. T dependence small.	Atkinson [1994]
$RO \rightarrow$ Products (decomp)	Small	Poor	T dependence significant. Method depends on knowledge of thermochemistry. Very uncertain at low temperature.	Atkinson and Carter [1991]
$RO \rightarrow$ Products (isomer)	None	Poor	Data are derived. T dependence very unreliable.	Atkinson [1994]
$RO_2 + NO \rightarrow RONO_2$ (RO + NO_2)	Moderate	Poor	Complex reaction. T dependence small. Method for estimating branching ratio for alkoxy radicals only.	Atkinson [1994]
$RO_2 + NO_2 \rightarrow RO_2NO_2$	Very small	Fair	Suitable to task. Data from reverse reaction also. Essentially T and P independent.	Atkinson [1994]

Table 5.3-2 summarizes our conclusion regarding the application of the estimation methods discussed here. The status comment is based on the utility of the method under temperature and pressure conditions encountered in the upper troposphere.

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Chapter 6

Global Modeling Initiative

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INTRODUCTION

The NASA Atmospheric Effects of Aviation Project (AEAP) has been charged with assessing the potential impact of existing and future aircraft on the global environment. The Atmospheric Effects of Stratospheric Aircraft (AESA) Phase I component of the High-Speed Research Program (HSRP), initiated in 1989, has addressed the potential chemical and climatic effects of a proposed fleet of supersonic civil aircraft flying in the lower stratosphere [Prather *et al.*, 1992; Stolarski and Wesoky, 1993a; Stolarski and Wesoky, 1993b; Stolarski *et al.*, 1995]. Phase II of this program continues to look at this problem, with specific emphasis on addressing current uncertainties in the Phase I assessment [Stolarski *et al.*, 1995]. The Subsonic Assessment (SASS) program will evaluate the chemical and climatic impact of the current and future fleet of civil and military subsonic aircraft.

Numerical models have been used successfully to translate our physical insights of the mechanisms operating in the atmosphere to quantitative results that can be compared both amongst themselves and against observations. These models are useful in assessment studies. The impact of a fleet of high-speed civil transports (HSCTs) on lower stratospheric ozone has been assessed by several two-dimensional (2-D) models (Figure 6-1). This past assessment effort also involved intensive model intercomparison and model-data comparison efforts [Prather and Remsberg, 1993 that pointed to both outstanding scientific issues and practical coding procedures which should be addressed in future assessments.

A credible assessment of the atmospheric impacts requires that these models provide accurate representations of the complex dynamical, radiative, chemical, and microphysical processes in the troposphere and stratosphere. The accuracy of the numerical algorithms must be tested by intercomparison of different approximations, while their realistic representation of atmospheric processes must be ascertained by suitable comparison to atmospheric observations. Past efforts have pointed out discrepancies both amongst current models and between model results and atmospheric data. Diagnosing the reasons for discrepancies amongst model results has proven to be a difficult task, due in part to the complete independence of the different models used, and the lack of common standards of coding and input/output which would facilitate isolating the differences in specific algorithms. Analysis of the discrepancy between model results and data is crucial to model improvement. This analysis would benefit from development of common diagnostics for model results, and direct intercomparison of the results of different algorithms. Not enough effort has been applied to attempt resolution of these issues because of the intense demands placed on the different modeling groups to produce results for the program.

The scientific issues in SASS and future AESA Phase II efforts involve processes which, ultimately, need to be simulated in three dimensions. Utilizing a three-dimensional (3-D) model in these assessments would tax the computational and personnel resources of individual modeling groups. The complexity of the scientific problems involved, and the size of the input and output data products would also make intercomparison and testing efforts much harder than for 2-D models. Addressing these challenges requires a new approach to the assessment effort. The AEAP Global Modeling Initiative described in this document is expected to improve the scientific quality of future assessments and also reduce the commitment of both personnel and financial resources to duplicate efforts.
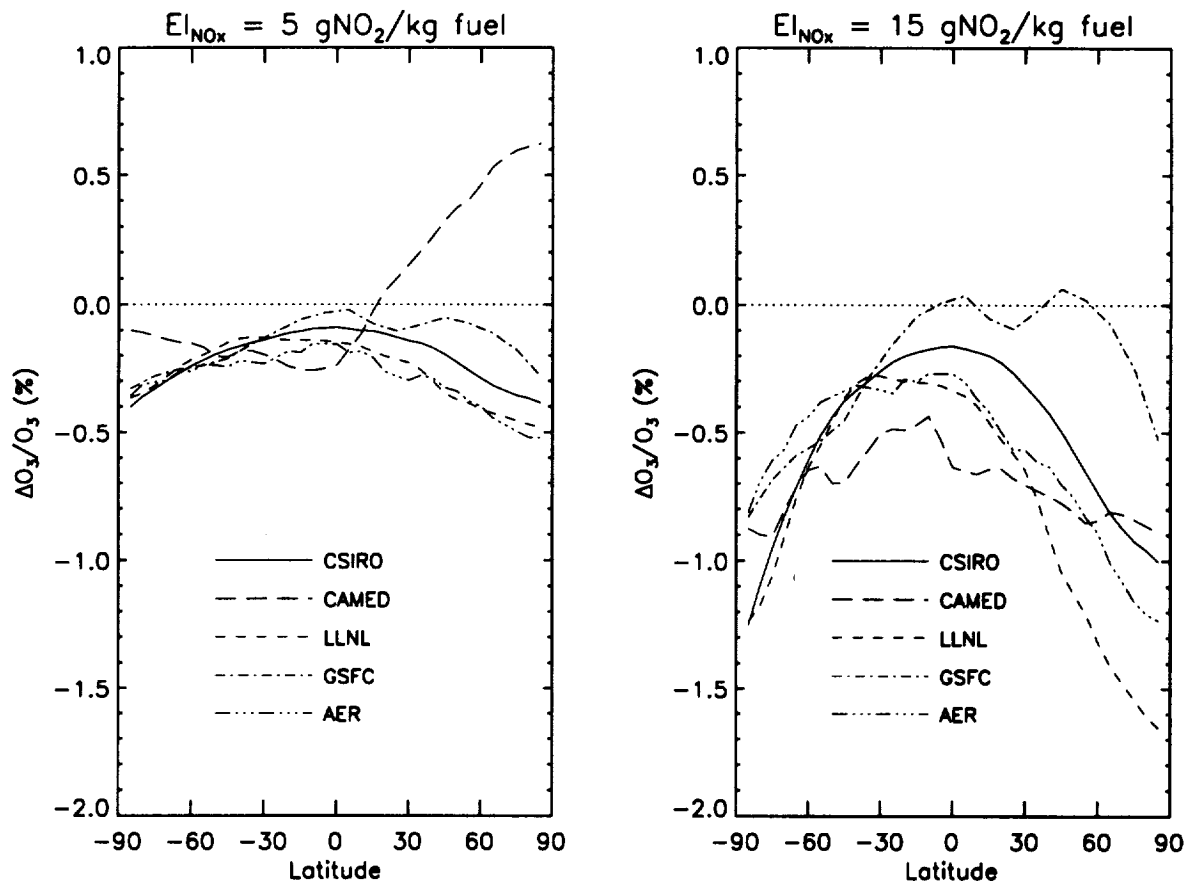
Figure 6-1. Calculated column ozone change (%) during March as a function of latitude for a Mach 2.4 HSCT fleet from the several models; a) EI_{NO_x} = 5 g NO_2/kg fuel, and b) EI_{NO_x} = 15 g NO_2/kg fuel. The changes reflect the difference between a calculation of the projected 2015 supersonic and subsonic fleets and the projected 2015 subsonic fleet in the absence of a supersonic fleet [Stolarski *et al., 1995*].

SCIENTIFIC ISSUES

Supersonic (Stratospheric) Aircraft Assessment

Although general agreement on the predicted impact supersonic aircraft will have on the atmosphere has increased in the past five years, significant differences still exist (Figure 6-2), pointing to the need for further work in model intercomparison. A National Research Council (NRC) Review Panel recommended that this program undertake a more extensive analysis of the reasons for these differences [NRC, 1994]. In addition, the Panel has recommended a more careful consideration of the uncertainties in present assessments. Many of these uncertainties stem from the limitations inherent in a 2-D simulation of the atmosphere. Others point to further developments in process models that need to be included in both 2-D and 3-D models.

The model-calculated ozone reductions depend on the following factors:

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- The amount and spatial distribution of reactive nitrogen (NO_y) and water (H_2O) in the stratosphere, both from natural and aircraft sources.
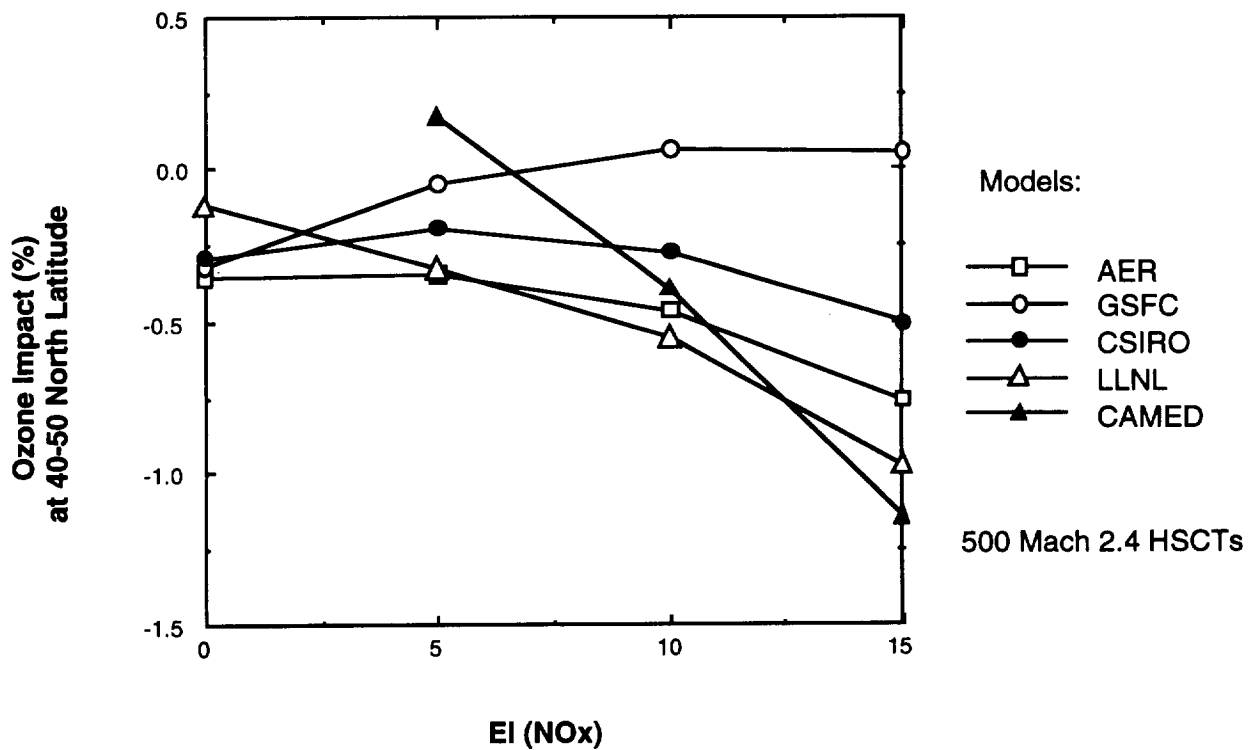
Figure 6-2. Predicted column ozone change (%) in the 40° to 50°N latitude band as a function of EI_{NO_x} for a fleet of 500 Mach 2.4 HSCTs [Stolarski *et al.*, 1995].

- The response of ozone to changes in NO_y and H_2O in the presence of aerosols and polar stratospheric clouds (PSCs).

- The potential change in aerosol loading and PSC formation due to injections of NO_y, sulfur, and water.

These factors point to the following issues to be considered in future assessments:

- Both 2-D and 3-D models simulate the exchange between the troposphere and stratosphere using large-scale transport by advection and diffusion. Local distributions of NO_y and H_2O depend on the details of this transport. Preliminary comparisons between 2-D and 3-D models (Figure 6-3) seem to indicate that: a) most of the stratospheric-tropospheric exchange in the 3-D simulation occurred at mid-latitudes where the aircraft effluents are deposited; in contrast, 2-D exchange occurs at higher latitudes, resulting in longer residence times in the lower stratosphere; and b) the 3-D simulation had a stronger upward transport of a fraction of the emitted NO_y. Since NO_y deposited at higher altitudes is more efficient in

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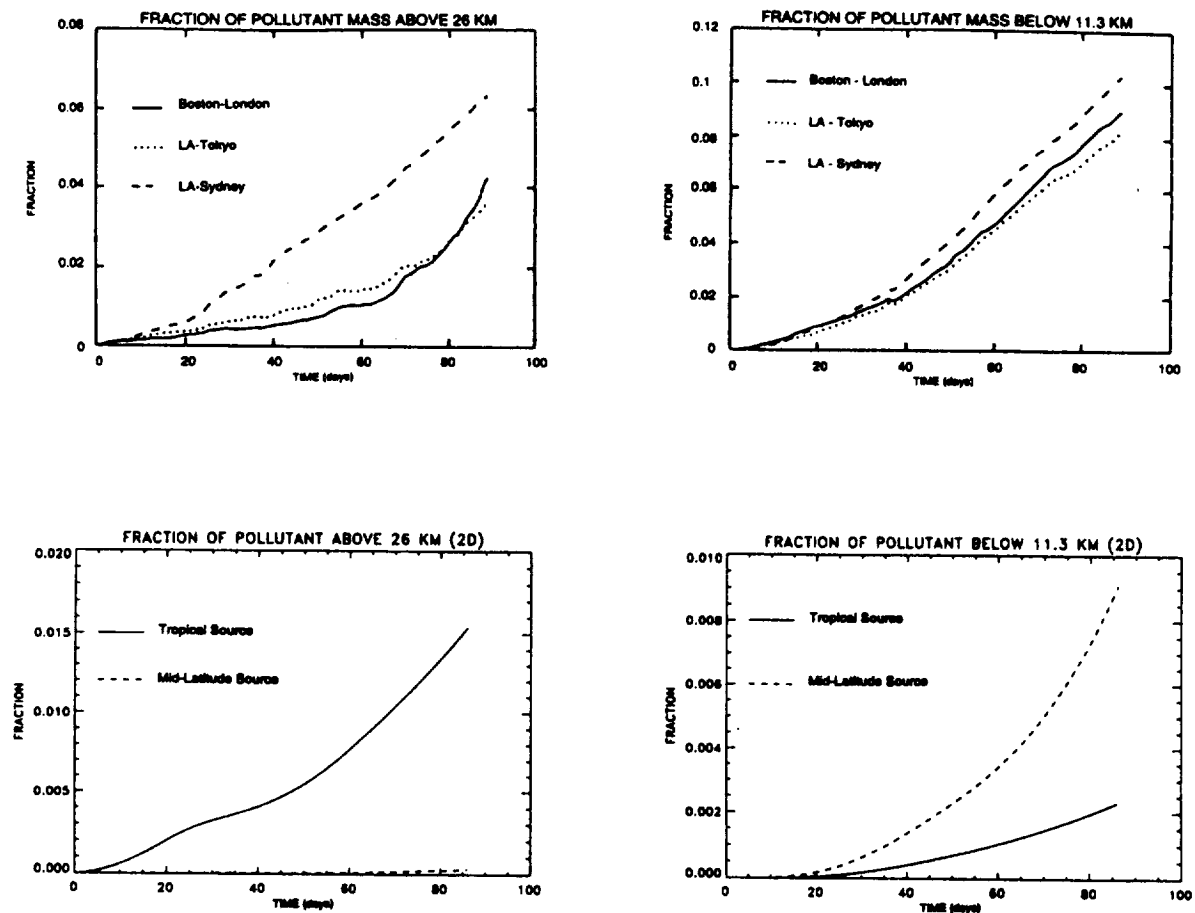
Figure 6-3. Fraction of aircraft pollutant above 26 km calculated by three-dimensional (top panels) and two-dimensional (bottom panels) models at NASA Goddard Space Flight Center. See Douglass *et al.* [1993] for details.

removing ozone, a stronger upward transport could increase the effect of HSCTs in removing ozone. However, it is not clear at this point how robust these conclusions are if we used other winds derived from different general circulation models (GCMs), or other data assimilation systems.

- The characteristics of subpolar and subtropical barriers to transport need to be understood to assess the fraction of effluent transported to tropical upwelling regions and polar vortices affected by heterogeneous chemistry.

- Heterogeneous reactions involving interaction of chlorine nitrate (ClONO$_2$), hypochlorous acid (HOCl), and hydrogen chloride (HCl) with aerosol and PSCs are very dependent on local temperature. Zonal asymmetries in temperature and atmospheric composition induce large nonlinearities in the rates of these reactions, which cannot be modeled by adopting a zonally averaged temperature and concentration field [Murphy and Ravishankara, 1994].

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- The interaction between injected NO_y and heterogeneous chemistry is uncertain. Analysis of the potential for PSC formation due to enhanced NO_y outside the vortex has been carried out by Considine *et al.* [1994] utilizing National Meteorological Center (NMC) temperature statistics and a 2-D model. The impact was found to be negligible. Deposition and/or transport of NO_y to within the Arctic vortex can lead to deactivation of chlorine monoxide (ClO) through formation of $ClONO_2$. At the same time, it could lead to enhanced PSC formation and/or denitrification, which would in turn increase the chlorine activation, and thus lead to additional ozone reductions. Our current best understanding of PSC formation and denitrification processes need to be represented in both 2-D and 3-D models.

- The sensitivity of calculated ozone changes to heterogeneous chemical reactions indicates the crucial role played by the atmospheric aerosol loading. The contributions of different natural and anthropogenic sources of sulfur need to be evaluated. In particular, the question of what is the truly "clean" background loading needs to be determined. The relative importance of particle production in aircraft plumes to the global aerosol layer needs to be addressed [Weisenstein *et al.*, 1996].

Subsonic Assessment

Current concern about the potential impact of subsonic aircraft focuses on the following issues:

- Nitrogen oxides (NO_x) in the aircraft exhaust could contribute appreciably to the total NO_x budget in the upper troposphere. Increases in upper tropospheric NO_x could then lead to increases in ozone.

- Sulfur, water and condensation nuclei emitted by the aircraft can lead to changes in upper tropospheric cloudiness, both by direct formation of contrails and indirect effect on cloud formation.

- Changes in upper tropospheric ozone and cloudiness could have an impact on global climate.

Preliminary studies [Johnson *et al.*, 1992; Hauglustaine *et al.*, 1994; Kasibhatla, 1993; Ehhalt *et al.*, 1992] have utilized 2-D and 3-D models to address some of the above issues. However, it must be pointed out that we still do not have tropospheric assessment models which include all mechanisms relevant to the upper troposphere, and whose results have been intercompared and tested against a whole range of atmospheric observations. In particular, further work is needed in the following areas:

- Tropospheric sources of NO_x and ozone precursors, both natural and anthropogenic, must be better quantified. In particular, large uncertainties still exist on the magnitude and distribution of NO_x production by lightning.

- The transport processes which affect the upper troposphere are complex. The implications of different winds and convective approximations need to be ascertained to evaluate the uncertainties in the NO_x response. Furthermore, the large-scale approximations of localized

processes such as convection and stratosphere-troposphere exchange need to be evaluated against both regional scale models and observations.

- The chemistry in the troposphere is more complex and uncertain, particularly in the evaluation of the impact of organic ozone precursors. Complete chemical schemes, including accurate treatment of aqueous chemistry and tropospheric radiation fields, need to be incorporated and intercompared. The chemical cycling of NO_x and ozone in the upper troposphere deserves better study.

- Nonlinearities in the NO_x-ozone chemistry imply that the production of ozone by an aircraft input of NO_x will depend on the scale over which the NO_x is injected; thus it is necessary to parameterize "effective" sources of ozone due to processes at the level of individual plumes. Particle production and contrails could directly affect the radiative budget, or lead to cirrus cloud formation.[1] Thus, small-scale mixing into the larger grid model scale must be evaluated.

- In contrast to the proposed supersonic transport, the effects of subsonic aircraft could have occurred over the last decades. Design of experiments aimed at detecting such signatures at different scales in the atmosphere will involve close interaction between the modeling and observations communities.

Research vs. Assessment Modes

We can identify two modes of operation for global models. In a research mode, investigators focus on specific mechanisms and algorithms. In most cases, simulations in this mode run for a period of weeks to a few years to test the model against observations. 3-D models have operated up to now exclusively in a research mode.

In an assessment mode, on the other hand, we have the following characteristics:

- The models must be able to run long assessment runs at a decadal scale, with alternative assumptions for sensitivity studies.

- Computational efficiency may require incorporation of approximations into these models.

- Model components must be tested against observations and against results of more complete research models.

It must be pointed out that specific research issues and/or benchmarks for testing approximations may require the running of "research" models for several years. However, sensitivity calculations considering multiple scenarios utilizing existing complete models would severely tax current computational and personnel resources.

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AEAP GLOBAL MODELING INITIATIVE

Goals

The primary goal of the initiative is to develop a multi-module, extensively tested, 3-D chemical-transport model to assess the impact of supersonic and subsonic aircraft. 2-D models will also be incorporated to supplement the assessment effort, and interface with the results of 3-D models.

Approach

The AEAP initiative seeks to develop the above model as a single modular structure, incorporating algorithms and databases from different groups (Figure 6-4). Specific characteristics and anticipated advantages of this approach are:

- The modular structure will be designed with a unified driver and standard diagnostics, and will allow carrying out assessment calculations and estimate uncertainties using different combinations of global winds, transport algorithms, and chemical parameterizations.

- Development of a modular structure will necessitate establishing common standards for input and output, format, data structures, and coding. Such standards will facilitate intercomparison of simulations and uncertainty analysis.

- The model will be developed, analyzed and tested under the guidance of a Science Team constituted by investigators concentrating on different research aspects of multi-dimensional modeling.
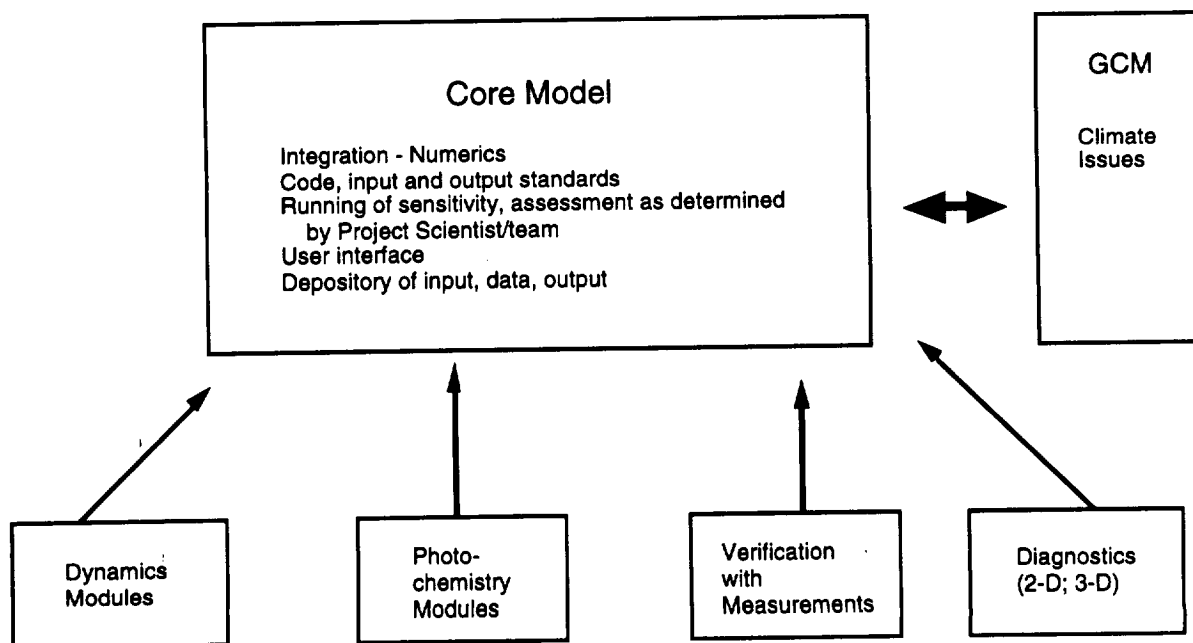

Figure 6-4. Schematic diagram of proposed 3-D model for AEAP.

- A "core" institution is selected to integrate and support the central model. This institution will also be responsible for carrying out the specific assessment runs, thus freeing individual team members to concentrate on research efforts. Team members will still be responsible for contributing to setting up and analyzing assessment runs.

- Science Team members will be funded for integration and analysis of the central model. Support will also be provided for continued research in their specific areas of expertise, but base funding from other agencies is expected to be used.

- Participation and collaboration in the Science Team will benefit not only the development and testing of the central model, but also the particular research interests of the participants through access to data bases, algorithms, and codes. This access will be facilitated as much as possible through the "core" institution, within the priorities established by the Science Team to accomplish AEAP goals.

- A strong emphasis will be placed on collaboration with the community making atmospheric measurements, both in terms of experiment design and in utilization of existing and forthcoming data bases for model verification.

MODEL COMPONENTS AND SCIENCE TEAM CONFIGURATION

This section describes the current and proposed activities of the Science Team for the Global Modeling Initiative, as constituted in early 1995. Comparison of the current activities and expertise with the scientific needs discussed above will necessarily point out areas for further development. It is one of the purposes of this description to elicit further interest in the scientific community, which would facilitate addressing these issues.

Activities of the Science Team fall under the following broad categories:

Circulation and Transport Schemes

The goals of activities under this area are:

- To provide existing winds and circulation diagnostics from both General Circulation Models and Meteorological Assimilation models.

- To provide accurate and efficient advective algorithms and convective schemes.

- To develop, in collaboration with the core institution, data formats, structures and interfaces which would allow simulations by the central model using different combination of winds and transport schemes.

- To test the results of the integrated model against the separate runs to ensure that the integration process has not corrupted results.

- To continue testing the incorporated meteorological fields and their transport of tracers against available measurements, and to update products delivered to the central model as improvements are introduced.

- To test the convective parameterizations and stratospheric-tropospheric exchange in global-scale models against higher-resolution formulations in regional models.

At present, the following winds and diagnostics will be provided by the team members indicated:

- Goddard Institute for Space Studies (GISS) GCM results: J. Hansen and D. Rind, GISS; M. Prather, University of California, Irvine (UCI)

- Community Climate Model-2 (CCM2): P. Rasch, National Center for Atmospheric Research (NCAR)

- Data Assimilation Office (DAO), Goddard Space Flight Center (GSFC): R. Rood, GSFC; D. Rotman, Lawrence Livermore National Laboratory (LLNL)

- European Center for Medium Range Weather Forecast (ECMWF) - UK: M. Prather; I. Isaksen, University of Oslo

The following advection algorithms will be available:

- Second-order moments: M. Prather

- Semi-Lagrangian scheme: P. Rasch

- Van Leer: D. Allen, GSFC; D. Rotman

- Flux-form Semi-Lagrangian scheme: Lin *et al.*, GSFC

Basic convective schemes are included in both the GISS and NCAR shells. Incorporation of several additional convective schemes is being implemented by P. Rasch. A convective scheme has recently been added to the Lin *et al.* GSFC transport shell. Testing of convective schemes and stratospheric/tropospheric exchange utilizing smaller-scales models will be carried out by C. Walcek, State University of New York (SUNY)/Albany (MM5); P. Hess and J. F. Lamarque, NCAR (MM5); and K. Pickering, University of Maryland/GSFC (MM5, Goddard Cumulus Ensemble Model).

J. Tenenbaum, SUNY/Purchase, will provide an expanded wind data set from aircraft measurements to improve operational analyses.

Chemistry

Activities under this category will provide the following:

- Photolysis and chemical schemes, including aqueous and heterogeneous chemistry, which have been both intercompared amongst themselves and against existing measurements. Parameterizations and/or approximations which improve the computational efficiency of the chemistry and would facilitate carrying out multi-year runs. [e.g., Spivakovsky *et al.*, 1990].

Interfaces between a given chemical scheme and the central model and/or other intermediate parameterizations.

- Intercomparison of stratospheric photochemical schemes is currently ongoing under the AESA Phase I effort. Aircraft measurements aboard the ER-2 now provide a complete set of tracer and short-lived species data which allows detailed testing of stratospheric chemistry against atmospheric observations (Figure 6-5).

- An efficient and accurate radiative code to calculate photolysis rates in the troposphere is needed. This code should account for different conditions of cloud coverage and type, ground albedo, and aerosol loading. Efforts towards this goal will continue to expand as the program progresses.

- Characterization of the different sources of NO_x and ozone precursors, and evaluation of large-scale representation of ozone production for aircraft plumes.

- Parameterizations for wet and dry deposition capable of being adopted in a global chemical transport model (CTM).

- Evaluation of uncertainties in the results of different process models due to uncertainties in input data, such as chemical kinetic rates, transport formulations, or emissions.

- Microphysical schemes which would allow evaluation of particle production, impact of aircraft emissions on background aerosols, and cloud formation.

Chemical mechanisms for the stratosphere will be contributed by M. Ko, Atmospheric and Environmental Research, Inc. (AER); G. Brasseur, NCAR; D. Jacob, Harvard; and Ross Salawitch, Jet Propulsion Laboratory (JPL).

Tropospheric chemistry mechanisms, including high-order hydrocarbons, aqueous chemistry, and simple parameterizations of tropospheric radiation fields will be contributed by C. Walcek; D. Jacob; and R. Ramaroson, Office National d'Études et Recherches Aerospatiales (ONERA).

Plume chemistry studies will be performed by M. Ko and C. Walcek.

Uncertainty analysis of given process models will be carried out by J. Milford, University of Colorado.

Stratospheric microphysical models will be contributed by G. Visconti, Universita' degli Studi l'Aquila; and M. Ko.

A parameterization of chemical mechanisms based on polynomial fitting of results from an arbitrary chemical/photochemical/microphysical model will be contributed by C. Spivakovsky, Harvard; and M. Ko.

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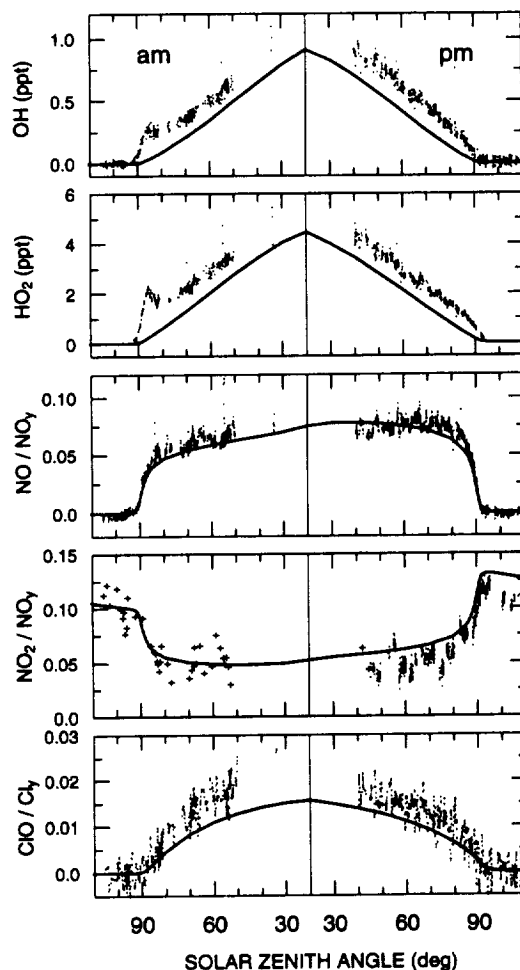
Figure 6-5. Diurnal variations of free radicals (OH, HO_2, NO, NO_2, and ClO) measured at 19 km, 37°N during the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE). The lines are calculations using a photochemical model [Salawitch *et al.*, 1994] indicating the presence of one or more unknown reactions producing HO_x in the atmosphere. The SPADE experiments, conducted in November 1992 and April, May, and October 1993, provided the first systematic measurements of stratospheric HO_x radicals, along with key radicals from other families and tracers of atmospheric transport, providing new understanding of stratospheric photochemical and dynamical processes. [Adapted from SPADE Special Issue, *Geophysical Research Letters*, Vol. 21, No. 23, November 15, 1994.]

Characterization of sources is currently being implemented by J. Penner and C. Price, LLNL (lightning sources); S. Baughcum, Boeing (aircraft emission scenarios); D. Wuebbles, University of Illinois (emission scenarios); and J. Logan, Harvard (emission inventories).

Parameterizations for wet and dry deposition will initially be taken from the work by D. Jacob and C. Walcek. These parameterizations would need to be adapted as different meteorological fields with different convective characteristics are incorporated.

Two-Dimensional Assessment Models

Although the primary goal of the initiative is the development of a 3-D model, assessment efforts scheduled over the next three years may require supplemental 2-D runs for interim results. These calculations would continue to address stratospheric perturbations. They also would specifically evaluate the limitations in use of 2-D and 2 1/2-D models (zonal mean chemistry transport models coupled with a semi-spectral dynamical model) in the troposphere. Participation in the global initiative would have the following goals:

- To continue support for assessment-grade 2-D and 2 1/2-D models.

- To incorporate results and diagnostics from appropriate tracer 3-D simulations.

- To provide assessment simulations as needed.

2-D modeling support will be provided by M. Ko; C. Jackman and D. Considine, GSFC; and D. Kinnison, LLNL.

Diagnostics from 3-D model simulations and interface with 2-D models will be carried out by M. Geller, SUNY/Stony Brook.

Climate Assessment

The assessment of climate impact is an extremely important long-range component of this effort. We must emphasize, however, that current personnel and funding limitations do not allow development of a GCM with coupled chemistry for assessment studies. Climate assessment with GCMs will be carried out off-line for a limited set of scenarios, and eventually incorporating as much as possible the input from the testing carried out under the CTM effort. It is expected that the climate component will increase in future years.

Climate assessment will be performed by D. Rind and J. Hansen at GISS.

Utilization of Atmospheric Observations

Atmospheric modelers have started to utilize the extensive dataset of atmospheric observations available from different platforms. Furthermore, future measurements missions will continue to benefit from input from the modeling community regarding measurements strategy which would best test model results. Thus, data utilization is expected to be an important component of the initiative. The goals of this task are to:

- Interface with existing data from ground-based, airborne and satellite platforms to test model transport, convection, stratospheric/tropospheric exchange, and chemistry.

- Determine and provide sets of existing observational data whose quality makes them suitable for model verification.

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- Derive diagnostics from measurements and models which facilitate model verification.

- Interface with the planning of future measurement campaigns to develop measurement strategies best suited for model verification.

The following investigators are currently in place in the initiative:

- A. Douglass, GSFC - Upper Atmosphere Research Satellite (UARS) data

- D. Jacob, J. Logan, and C. Spivakovsky, Harvard University - Tropospheric ozone and precursor, tracers of transport

- D. Kinnison, LLNL - Radionucleides

- M. Prather, UCI - Tracers, strategies for model verification

- R. Salawitch, JPL - Testing against aircraft, balloon, and Atmospheric Trace Molecule Spectroscopy (ATMOS) data

We envision this to be an area of continuous expansion throughout the initiative. In particular, utilization of the extensive set of measurements collected by aircraft, balloon, and shuttle platforms will be emphasized. Aircraft data has proven useful in constraining photochemical mechanisms in the stratosphere [Salawitch *et al.*, 1994]. Recent CO_2 measurements from the SPADE mission points toward the potential for constraining transport rates in the stratosphere through examination of the propagation of the seasonal and secular signals (Figure 6-6) [Wofsy *et al.*, 1994; Boering *et al.*, 1994; Hall and Prather, 1993]. Interaction and utilization of data from future aircraft campaigns (e.g., Stratospheric Tracers of Atmospheric Transport (STRAT)) will capitalize on the potential of these measurements.

Core Institution/Model

The central model will reside at LLNL. Douglas Rotman is the Global Model Initiative (GMI) Project Manager, responsible for overall integration and running of the central model. The scientific direction of the Science Team will be coordinated by the GMI Project Scientist, Jose M. Rodriguez of AER, Inc.

The team at the core institution will be responsible to do the following:

- Develop a central shell structure, input/output formats and coding standards for the central model.

- Collaborate with Science Team members in the integration of different modules.

- Carry out test and assessment runs as authorized by the Project Scientist in consultation with the Science Team.

The structure of the core shell will initially be adapted from the structure developed at LLNL for their IMPACT CTM. The main characteristics which make this structure attractive are implementation of modularity, design for single and multi-processor platforms, portability to different platforms, and current expertise at LLNL.

Due to the vast computational requirements envisioned for the assessment efforts, strong emphasis will be placed in developing this model for massive parallel architectures. Work during the first year will utilize computational resources at LLNL. Efforts are in progress to identify additional computing platforms for further development and production efforts.

FUTURE PLANS AND LONG-TERM GOALS

Science Team Expansion

The present constitution of the Science Team is summarized in Table 6-1, and the specific contributions of each member in Tables 6-2 through 6-5. Participation in the Science Team is envisioned to be open on a regular basis to new participants. The main criterion for inclusion is the ability to contribute a specific algorithm, analysis tool, or data base to the effort on an ongoing basis.

Request for participation in the Science Team can be addressed in a letter format to the GMI Project Scientist specifying proposed project, relationship to ongoing activities, personnel involved and duration of effort. The Project Scientist will communicate requests and new membership to the rest of the team. We stress that such requests would be for participation in Science Team only. Funding for specific tasks involved in Science Team needs to be requested from the appropriate agencies through the usual channels.

We also encourage participation in Science Team meetings by other investigators involved in similar areas of research. The current 3-D initiative will profit from intercomparison and discussion with other modeling efforts both within and outside the United States. We anticipate two full Science Team Meetings per year, both in the U.S. Requests for participation and presentations at a Science Team meeting should be addressed to the GMI Project Scientist.

Long-Term Goals

The AEAP initiative is envisioned to last until 2001. Priorities for specific tasks will be determined by the future assessment deadlines and planned measurement campaigns. Specifically, the activities over the next three years will be guided by:

• SASS interim assessment in 1996.

• STRAT aircraft campaign in 1994-1996, other possible campaigns yet to be defined.

• AESA Phase II assessment in 1998.
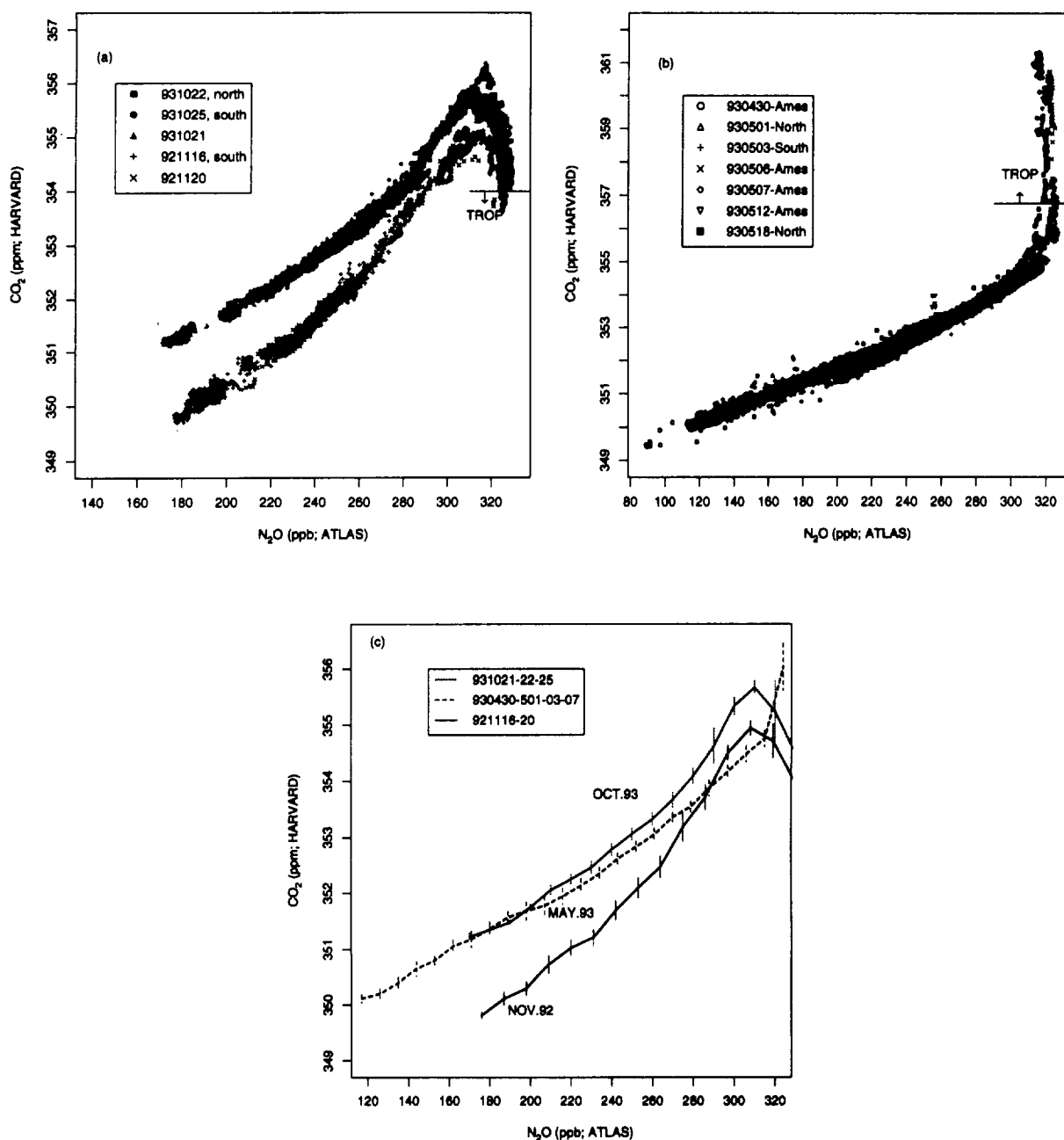
Figure 6-6. Correlation plots for simultaneous measurements of CO_2 and N_2O from the NASA ER-2 aircraft during SPADE: (a) fall 1992 [20°N-42°N] and fall 1993 [17°N-61°N]; (b) spring 1993 [14°N-61°N]; (c) CO_2 binned and averaged as a function of N_2O in 10 ppb intervals from (a) and (b). The meteorological tropopause with respect to CO_2 values is marked. Most outliers above the correlation curves correspond to detection of ER-2 exhaust. Other outliers may be due to instrument time discrepancies on the order of 1 or 2 seconds and/or real deviations in the atmosphere. [Adapted from Boering et al., 1994].

Table 6-1. Science Team for AEAP Global Model Initiative.

Project Scientist: J. M. Rodriguez, AER, Inc.
Project Manager: D. Rotman, LLNL

Principal Investigator	Institution	Co-Investigators
Baughcum/Wuebbles	Boeing/U. Illinois	
Brasseur	NCAR	Hess/Lamarque/Madronich
Douglass	NASA/GSFC	Rood/Jackman/Weaver/Cerniglia
Geller	SUNY/Stony Brook	
Hansen/Rind	GISS	
Isaksen	U. Oslo	
Jackman	NASA/GSFC	Considine
Jacob/McElroy	Harvard	Logan/Spivakovsky/Schneider/Salawitch
Kinnison	LLNL	
Ko	AER	Danilin/Kotamarthi/Shia/Weisenstein/ Portman/Sze
McConnell	York University	Kaminski
Penner	LLNL	Price
Pickering	GSFC	Tao/Scala/Lin/Rood/Douglass
Prather	UCI	
Ramaroson	ONERA	
Rasch	NCAR	
Rood	GSFC	Douglass/Pickering
Rotman	LLNL	Tannahill/Bergmann
Salawitch	JPL	
Tenenbaum	SUNY/Purchase	Geller
Visconti	U. l'Aquila	
Walcek	SUNY/Albany	Milford/Stockwell

R. Stolarski, A. Thompson, R. Friedl serve as ex-officio members.

Table 6-2. Winds-transport algorithms.

Principal Investigator	Tasks
Hess/Lamarque	Test stratospheric-tropospheric exchange
Hansen/Rind	Feedback to GISS
Isaksen	ECMWF
McConnell	University of York CTM
Pickering	Convective algorithm (tested); Flux-form Semi-Lagrangian shell
Prather	GISS winds; second-order moments - Shell
Rasch	CCM2 - Semi-Lagrangian shell
Rood	DAO winds- Van Leer shell
Rotman	Core shell
Tenenbaum	Aircraft meteorological fields for DAO
Walcek	Convection - Deposition algorithms

Table 6-3. Chemistry-sources-deposition.

Principal Investigator	Tasks
Brasseur	Stratospheric chemistry module
Isaksen	Stratospheric/tropospheric chemistry module
Jacob	Stratospheric/tropospheric module Aqueous chemistry
Ko	Stratospheric chemistry module Parameterization Plume chemistry
Penner/Price	NO_x sources
Ramaroson	Stratospheric chemistry
Visconti	Microphysics
Walcek	Boundary layer chemistry Uncertainty analysis Plume chemistry
Kinnison	Fast Gear code
Baughcum/Wuebbles	Emission scenarios

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Table 6-4. Model verification against atmospheric data.

Principal Investigator	Tasks
Douglass	UARS data
Jacob/Logan/Spivakovsky	Tracers of transport Tropospheric ozone and precursors
Kinnison	Radionucleides
Salawitch	Aircraft, balloon, ATMOS
Prather	3-D tracers

Table 6-5. Other assessment efforts.

PI	Task
Geller	3-D diagnostics/comparison to 2-D
Hansen/Rind	Off-line climate impact sensitivity studies
Jackman	2-D
Kinnison	2-D
Ko	2-D; 2 1/2-D
Isaksen	2-D
Visconti	2-D

Although, we do not anticipate a strong 3-D component for the SASS interim assessment, we expect to participate in both limited 3-D calculations and 2-D sensitivity studies. The full 3-D assessment model is expected to be operational to participate in the 1998 AESA Phase II assessment. Efforts during the first three years will emphasize the stratospheric component of the model. However, the complexity of the issues involved in subsonic assessment will require immediate start on testing of convective parameterizations and tropospheric chemistry.

A preliminary time-line for activities for the next three years is given in Figure 6-7.

Model Availability

The model code will be made available to the community after sufficient testing and utilization would warrant its release. Without the experience in model development to be gained over the next year, no firm date for public release can be made at this point. Utilization of the model in the interim will be restricted to tasks related to the AEAP initiative. Requests for specific simulations must be approved by the GMI Project Scientist in consultation with the Project Manager and advisors appointed from the Science Team.

	1995	1996	1997	1998
Initial Wind Integration - (2 GCM, 1 DAO)	➤			
Initial Chemistry Integration	➤	➤		
Strat Simulations	═══════════════►			
SASS Preliminary Assessment		═══════►		
Chemistry Optimization - Testing		═════►		┄┄►
Integration of Additional Winds, deposition, Tested Convective Shcemes		═════►		┄┄►
Expanded Chemistry (Troposphere Aqueous,Tropospheric Photolysis Rates)		┄┄┄┄┄┄┄┄┄┄┄┄┄┄┄►		
Intercomparison Testing with Other Models - Verification with Data		═════════►		┄┄►
Stratospheric Assessment			═══════►	

Figure 6-7. Time line for global model initiative.

AESA-related ➤

SASS-related ➤

We expect that Science Team members will have access to data bases, algorithms, model results and the whole code as it evolves. Such access is deemed important to facilitate model analysis and testing by Science Team members.

Science Team members will also enjoy the benefit of being able to use these products in other research. However, this use is to be guided by the following principles:

- Use of any individual data or coding product for purposes outside AEAP must be approved by the person(s) originating this product. Co-authorship in any publications should be offered to these contributors.

- Further documentation/analysis of specific products or codes for purposes other than those of the AEAP project is left to the discretion of the individual researchers.

- A similar philosophy holds for the whole core model. Any use of this code by Science Team members prior to its release must be approved by the code originators, which in this case is the whole GMI Science Team. Documentation of the core model will proceed as the code develops, always guided by the needs of the AEAP initiative.

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- The Global Modeling Initiative cannot provide computing and/or personnel resources for individual research projects of Science Team members, unless such projects are deemed relevant to the AEAP goals by the Project Scientist in consultation with Science Team members.

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Chapter 7

Observations Overview

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PREAMBLE

Attempts to observe the impacts of subsonic aviation on the atmosphere are not new [Kuhn, 1970; Knollenberg, 1972; CIAP, 1975; Changnon, 1981]. The effect of contrails, primarily on local and regional atmospheric water vapor and cloud formation, was studied fairly intensively in the early 1970s. Contrail formation over Europe has been probed more recently [Schumann and Wendling, 1990]. Thus, the effect of soot and sulfur dioxide (SO_2) gas-to-particle conversion on contrail formation, aerosols and radiative forcing is a major area of the Subsonic Assessment (SASS) Observations activity. Section 7.1 summarizes observational approaches to the radiative and chemical impacts of subsonics. Section 7.2 is an excerpt from an aircraft mission plan detailing a particle-cloud-contrail-radiation oriented field program called SUbsonic aircraft: Contrail and Cloud Effects Special Study (SUCCESS).

More recently, attention has been focused on nitrogen oxide (NO_x) emissions. The effect of NO_x on ozone has been the focus of evaluating stratospheric effects of supersonic aircraft and of subsonics, for which 30 to 40% of exhaust is stratospheric [Stolarski and Wesoky, 1995]. Preliminary studies of subsonics effects include one-dimensional (1-D) and two-dimensional (2-D) models [Beck et al., 1992; Johnson et al., 1992] and a set of observations that points to significant upper tropospheric aircraft NO_x [Ehhalt et al., 1992]. The motivating questions for determining whether or not subsonics perturb upper tropospheric/lower stratospheric (UT/LS) NO_x and ozone are described in Table 1-2.

Not surprisingly, the largest element of SASS in terms of human and financial resources is Observations. As described in Chapter 1, there are two types of field programs. First, together with NASA's Atmospheric Effects of Stratospheric Aircraft (AESA) program and Upper Atmosphere Research Program (UARP), SASS is co-sponsoring the Stratospheric Tracers of Atmospheric Transport (STRAT) aircraft campaign to determine transport and residence times for NO_x and tracers (e.g., carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4)) in the UT/LS. Second, three intensive "process" field campaigns are scheduled for fiscal years 1996, 1997, and 1999. Findings from these missions will contribute to the regularly scheduled international assessments on ozone depletion, performed under the auspices of the United Nations Environmental Programme/World Meteorological Organization (UNEP/WMO), and climate change, conducted by the Intergovernmental Panel on Climate Change (IPCC). Thus, SUCCESS will take place before the first SASS Program assessment to be completed in 1996 and results will be incorporated into the 1998 UNEP/WMO ozone assessment (see Table 1-1). A chemical mission with a focus on reactive nitrogen (NO_y) measurements in aircraft corridor regions is planned for 1997.

Background: General Considerations for SASS Observations

In the course of the numerous workshops (Table 1-3) conducted to design observational strategies for SASS, the following factors were considered:

Scope of experiments - As mentioned in Chapter 1, the present knowledge of the UT/LS, subsonics effects and current (and developing) technology limit objectives to answering a few well-posed questions.

Climatology vs. process studies - The fact that stratospheric and tropospheric chemistry, dynamics, and radiative processes are least understood in the region of subsonic emissions (the tropopause ±4 km) complicates assessment of possible aircraft effects. Natural composition and variability of this region have not been well-characterized, and this has been argued as the basis for a climatological approach to experiments. On the other hand, as an issue-oriented program, SASS cannot simply extend climatology or conduct traditional "regional" studies without focusing on aircraft-related mechanisms. Thus, SASS-sponsored missions will strike a balance between nailing down small-scale processes and collecting the background data required to put perturbations in perspective (Figure 7-1). Recommendations from a workshop held in February 1994 to consider commercial platforms as a mechanism for amassing a physical (winds, temperature) and constituent (e.g., ozone, H_2O) climatology appear in Section 7.3. To date this approach has not been adopted by SASS.

Relationship to other experimental programs - There are a number of U.S. programs within NASA (AESA, UARP, Global Tropospheric Experiment (GTE), Radiation Processes) and beyond (e.g., those sponsored by the National Science Foundation (NSF), the National Oceanic and Atmospheric Administration (NOAA), and the Department of Energy (DOE)) that are studying the UT/LS and on which SASS research is building and seeking cooperation. Likewise, in formulating a chemical mission, SASS anticipates cooperation with the International Global Atmospheric Chemistry Programme (IGAC) experimental structure and with non-U.S. programs studying subsonics effects. Through the NASA Research Announcement (NRA) selection process, SASS missions are open to non-U.S. scientists on a non-funded basis. This strategy emphasizes the fact that SASS benefits from ongoing basic scientific programs and is undertaking assessment in an international context.

Instrument and platform technology - Technology issues have been uppermost in Observations planning [Baumgardner and Thompson, 1994]. Both instrument and platform readiness issues were studied in planning workshops in late 1993 and early 1994 (see Table 1-3). The ER-2 and DC-8, mainstays of NASA airborne experiments, have greatest operational flexibility at 20 km and in the 8-to 12-km range, respectively, just above and below critical regions for subsonics. (Recent STRAT ER-2 flights in October and November 1995 have demonstrated some capability below 15 km). Unmanned aerial vehicles (UAVs), which could offer good access to the UT/LS, are yet not available for SASS. In addition, the payload weight and volume for most UAVs is too limited for process studies requiring a large suite of species measurements. The WB-57F, an NSF- and NOAA-sponsored platform, which has ideal range for UT/LS studies, will be operational in 1996 for a limited geographical region. Formal SASS coordination with NSF- and NOAA-sponsored missions could follow. Two instrument issues have affected SASS planning: concerns about NO_y measurements in the UT [Crosley, 1994] and limitations in measuring particle morphology and composition. Platform availability and the development of new particle instrumentation (Section 7.2) have made it possible to schedule SUCCESS in early 1996. The status of total NO_y measurements in the UT/LS remains controversial [Crawford *et al.*, 1996]. An ideal "solution," which appears technologically feasible only near the end of SASS or beyond, is the development of reliable instrumentation for all principal NO_y components beyond nitric oxide (NO): nitrogen dioxide (NO_2), nitric acid (HNO_3), peroxyacetyl nitrate (PAN), organic NO_x, and peroxynitric acid (HNO_4). In the meantime, NO_y measurements will be eval-

SASS Observations

SASS Process Studies

> Chemistry - Contrails /Cirrus Study (SUCCESS-96)
> Wake/Plume Experiment (SNIF-96)
> NOx and Ozone Studies

Other Programs

> Non-US - STREAM, POLINAT, AERONOX
> UARP, AESA - Polar Studies, Lower Strat.
> GTE - Pacific Mission (91,94)
> GTE - Tropics (85,87,92,96,98)
> NSF - STERAO-96
> DOE - ARM
> IGAC - NARE, ACE

SASS Climatology

> Tracer Experiments with
   AESA, UARP (STRAT, 95-98)
> Commercial Platform
   Experiments (TBD?)
> Operational Satellites

Mechanisms (vertical axis)

Mapping (horizontal axis)

Figure 7-1. SASS Observations, showing dual approaches of process studies and adding to climatology. Relationship to other U.S. and international programs is also indicated.

uated with intercomparisons, where feasible, and by tracer correlations and determination of the so-called "shortfall" (the difference between an NO_y measurement and the sum of its constituents). New instrumentation for gaseous and particulate HNO_3 is expected in 1997. A related development, which is key to NO_x lifetime determination, is that an airborne hydrogen oxide (HO_x) instrument is operational on the ER-2. In 1996, testing and deployment of other HO_x instruments will be performed on the NASA DC-8 and C-130. However, no intercomparisons among airborne HO_x instruments have been made. Some degree of intercomparison is essential for evaluating experimental uncertainties.

Aircraft "signal" in existing data - There have been a number of aircraft missions in the UT/LS which have taken SASS-relevant measurements with high-quality instrumentation since 1990. NASA-sponsored missions, all with publicly archived data, include the Pacific Exploratory Missions (PEM-West A/B), Transport and Atmospheric Chemistry near the Equator - Atlantic (TRACE-A), Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA), the second Airborne Arctic Stratospheric Experiment (AASE II), Stratospheric Photochemistry, Aerosols and Dynamics

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Expedition (SPADE), and the First ISCCP (International Satellite Cloud Climatology Project) Regional Experiment (FIRE). The fast-SASS projects and a limited number of those selected through NRA competition included in-depth analyses to search for subsonics signatures in some of these data sets.

Archiving and accessibility of data - SASS experiments will follow standard practices of NASA data protocol, i.e., short- term, restricted (< 1 year) availability to mission Science Team principal investigators (PIs), with public posting in a NASA distributed active archive center (DAAC) and/or through issuance of a CD-ROM. This will allow modelers working on the Global Modeling Initiative (GMI) and other scientists worldwide timely access to data. Despite a plethora of NO_x and NO_y measurements in the troposphere, these observations have not been incorporated into global models to help evaluate the aircraft contribution to the NO_y budget relative to surface sources and lightning. To facilitate this activity, a major archiving of quality-checked, previously unavailable NO_x and NO_y data has been performed by Emmons and Carroll [1996]. Summary maps are presented in Section 7.4, along with a description of how to access these data sets. This archive will grow as new missions are conducted.

Interaction of models with experimental data - Meshing theory and experiment interactively in the field has been a successful strategy for UARP, GTE, AESA, and other programs. For SASS, experimental strategies will be developed so that process models are an integral part of the design, with each model selected to answer a key question defined in the mission plan. Careful experimental design optimizes data collection for validation, interpretation and uncertainty analysis by global models. Mission strategies and data analysis will also be coordinated with the GMI.

Of the several workshops convened to recommend experimental strategies, only the one held in Boulder, Colorado, on 5-6 January 1994 considered the broad range of potential missions required to answer the key SASS Observations questions. A workshop report [Baumgardner and Thompson, 1994] presents all the issues and discussion of that meeting. Section 7.1 is based on the measurement strategies section of the workshop report. For additional background on the formulation of the science question, instrument and platform readiness issues, the reader is referred to the full report.

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Section 7.1

Workshop Summary: Aircraft Mission Measurement Strategies for the NASA Subsonic Assessment Project

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PREAMBLE

This section is an excerpt from the Subsonic Assessment (SASS) aircraft mission measurement strategies workshop report prepared by Darrel Baumgardner and Anne Thompson [Baumgardner and Thompson, 1994]. Section numbers, designated as "WR," are as they appear in the report. The goal of the workshop, which was held 5-6 January 1994 in Boulder, Colorado, was to formulate potential measurement strategies in the context of the key scientific questions posed by the SASS program. The list of attendees is included at the end of this section. Requests for a copy of the complete workshop report, NCAR Technical Note NCAR/TN-411+PROC, should be sent to darrel@ncar.ucar.edu.

WR3. Measurement Strategies

The intent of the individual sessions on measurement strategies was to identify flight scenarios that would place aircraft in critical regions at the appropriate time and with the necessary instrumentation to acquire data that will address some of the primary questions listed above. The nature of the problems in the three areas of study are somewhat different, however, and were approached quite differently by each of the working groups.

WR3.1 Atmospheric Chemistry Missions

The fundamental problem in assessing the effect of aircraft emissions on ozone, sulfur species, and soot in the upper troposphere/lower stratosphere (UT/LS) is to evaluate the contribution of various sources of ozone precursors, sulfur oxides (SO_x), and soot relative to aircraft emissions in this region. The largest tropospheric sources of these trace gas species are anthropogenic and natural emissions in the boundary layer. In the case of nitric oxide (NO) lightning is an important UT source. Consequently, it is imperative to understand the role of vertical transport processes, particularly convection. Likewise, downward transport from the stratosphere provides another important source for reactive nitrogen (NO_y) and ozone in the UT/LS. Thus, in addition to seeking aircraft emission signatures, SASS must first assess the relative contribution to the UT/LS of nitrogen oxides (NO_x), SO_x, carbon monoxide (CO), and hydrocarbons from sources other than aircraft. There are limited flight hours available for climatological assessments of this type, so studies to conduct this type of assessment will require prioritization of two types:

(1) Using models and previous studies, determine which of the aircraft-emitted species are likely to have the largest effect on climate modification. This takes the form of a sensitivity study to determine what aircraft exhaust components can be most easily detected in both the near and far field environment. Focus measurement strategies on instrumentation that will provide redundant information on the highest priority species and then select flight profiles in regions where exhaust signatures can be most easily assessed.

(2) Using models and previous studies, determine the range of conditions that determine the range of variability in the selected trace gases. Select flight profiles that place the aircraft in those regions during periods when the variability is most likely to fall within this range and accumulate statistics that sufficiently characterize this variability.

There are basically two types of chemically oriented aircraft missions needed for subsonic assessment: climatology and process or budget studies to determine the relative magnitude of the aircraft source.

Mission 1: NO_x Budget Evaluation from Aircraft

Science Objectives:
- In the upper troposphere, how much NO_x is from lightning, aircraft emissions, stratospheric injection, and convective transport of boundary layer pollution?
- What is the seasonal and latitudinal variation in this budget?
- What is the partitioning of odd nitrogen among longer-lived species?
- Over major Northern Hemisphere aircraft corridors, how do aircraft emissions of NO_x (and their impact on ozone) compare with outflow from major continents?

Approach:
- Conduct missions in regions with deep convection, surface and aircraft sources, and lightning to characterize processes and budget. Start with Northern Hemisphere (U.S.-based) mission in region with frequent deep convection and with access to aircraft corridor.
- Follow-on mission in tropics (in region free of biomass burning) to characterize lightning source in low-pollution, aircraft conditions.

Payload Requirements:
- Sample range - 1000 to 300 mbar (100 mbar in tropics). Need two or three planes to cover convective clouds in inflow and outflow regions.
- Constituents - ozone, NO, NO_x, NO_y, peroxyacetyl nitrate (PAN), nitric acid (HNO_3), CO, methane (CH_4), hydrocarbons, hydrogen peroxide (H_2O_2), hydroxyl radical (OH)
- Meteorological data - Lightning network, temperature, winds, radar, ultraviolet (UV) flux; convective system needs ground-based support.

Note that global assessment of the lightning contribution will require extrapolation from process studies to global scale using satellite detection of lightning. Improved knowledge of different lightning types and NO production efficiency in lightning must develop simultaneously.

Mission 2: Climatology of NO_x, SO_2, aerosols, and ozone in UT/LS

Science Objectives:
- What is the variability of NO + NO_2 (NO_x) and of major reservoir species (HNO_3, organic nitrates, PAN) in the UT/LS?
- Do soot and sulfur dioxide (SO_2) from subsonics modify background concentrations in the UT/LS significantly?
- Do CO and hydrocarbons from subsonics modify background concentrations in the UT/LS significantly?

The science objectives and approach outlined here are nearly identical to the Stratospheric/ Tropospheric Exchange (STE) missions on tracer variability [e.g., see The tropical experiment of

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the Stratospheric-Tropospheric Exchange Project (STEP Tropical), *J. Geophys. Res.*, STEP special issue, 98, 8561-8773, 1993]. They can be accomplished in coordination with Atmospheric Effects of Stratospheric Aircraft (AESA) post-SPADE AESA tracer missions which were defined during and after the workshop. For more definitive species assignment, UARP DC-8 and/or ER-2 missions and GTE DC-8 missions that include radicals as well as tracers will expand climatology and provide some of the answers to these questions.

A SASS- and GTE-sponsored workshop on the state of NO_y instrumentation held in December 1993 highlighted instrument problems in NO_y, HNO_3, and NO_2 measurement at levels typical in the UT [Crosley, 1994]. Tests are underway to isolate causes and to determine accuracy of available techniques in terms of assessment requirements. This issue needs to be resolved before a definitive assessment can be made.

WR3.2 Stratospheric/Tropospheric Exchange (STE) Missions

STE processes do not lend themselves easily to aircraft studies. The primary focus will be to identify the primary sources, sinks, and fluxes of pollutants. Sinks in the UT/LS are moderately small-scale features (i.e., folds in the tropopause or deep convection), which lend themselves to aircraft investigations. The objectives of these missions will overlap to a certain degree with those of the chemistry missions summarized above in WR3.1. Three possible missions should be considered:

Mission 1: Tracer Variability Assessment

Science Objectives:
- What is the observed trace gas variability in the lower stratosphere/upper troposphere?
- What is its seasonal and latitudinal dependence?
- Can we identify the background structure of the stratosphere and troposphere, and can we identify the products of STE in both the stratosphere and troposphere?
- How does the trace gas variability orient itself to the observed meteorological structure?
- Can the transport models simulate these products of STE?

Approach:
Survey equator to pole during different seasons with a compliment of long-lived trace-gas measurements which show characteristics of the stratosphere and troposphere sources, urban sources, and aircraft sources.

Payload Requirements:
Sample range - 500 to 50 mbar
Constituents - ozone, water (H_2O), CO_2, N_2O, CFC-11, condensation nuclei (CN), carbon tetrachloride (CCl_4), CH_4, NO_y, Beryllium-6 (^6Be), aerosols
Meteorological data - temperature, winds, change in temperature with altitude

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Mission 2: Fold Transport Experiment

Science Objectives:
- Look at trace gases transported during fold evolution.
- Are mesoscale model computations of transport consistent with observations?
- Estimate diabatic processes which are important in fixing transport?
- Does clear air turbulence near the jet core create potential vorticity and allow tropospheric material to be entrained in the stratosphere?

Approach:
Forecast or identify a fold event and make series of measurements upstream and downstream during cyclogenesis and cyclolysis.

Payload Requirements:
Sample range -	500 to 50 mbar
Constituents -	ozone, H_2O, CO_2, N_2O, CFC-11, CN, CCl_4, CH_4, NO_y, aerosols
Meteorological data -	temperature, winds, change in temperature with altitude, infrared (IR) flux

Mission 3: Cloud Transport of Aerosols and Gases

Science Objectives:
- Can cumulus overshoot transport pollutants into the stratosphere?
- How does NO_y from lightning contribute to the overall NO_y budget which is also being perturbed by aircraft?
- How do surface emitted pollutants contribute to the upper tropospheric variability?
- Is stratospheric air transported downward at the edge of the anvil?

Approach:
Fly both upstream and downstream of the anvil sampling trace gases. Fly below anvil of large cumulus complex to estimate radiative flux (diabatic heating).

Payload Requirements:
Sample range -	40,000 to 60,000 ft, plus profiles to the boundary layer for initializing and validating models.
Constituents -	ozone, H_2O, CO_2, N_2O, CFC-11, CN, CCl_4, CH_4, NO_y, NO, NO_2, H_2O_2, methyl peroxide (CH_3OOH) (the H_2O_2/CH_3OOH ratio is a good indicator of cloud processed air), aerosols
Meteorological -	temperature, winds, change in temperature with altitude, IR flux

Additional needs:
Radar coverage (preferably dual Doppler)
Wind profiles
Lightning detection network

WR3.3 Cloud Microphysics/Radiation Missions

The types of aircraft missions that would address the microphysical and radiation questions posed by SASS are relatively straight forward and are much more process-oriented than those described for chemistry and STE missions. This is not to say that there is no climatological component, but rather that the questions to be addressed are somewhat more focused and lend themselves to better defined aircraft studies.

The recommended approach in planning these missions is to evaluate which perturbations caused by current or projected aircraft emissions can be dismissed as negligible and then direct SASS program efforts towards measuring those effects that cannot be dismissed.

While "radiative forcing" is a convenient primary measure of potential effects, other consequences of perturbations should also be considered. These might include dynamic consequences of redistributed radiation, possible changes in "seeder-feeder" systems or in other ice-phase precipitation, and modifications of the water vapor cycle caused by perturbed sedimentation rates of cirrus crystals.

The following missions were suggested for inclusion in the SASS field programs, with no specific order of priority:

Mission 1a: Emission/Plume Characterization, Single Aircraft

Science Objective:
Observe emissions from a single-aircraft by penetrating the plume. Options include circular or racetrack patterns.

Mission 1b: Emission/Plume Characterization, Two Aircraft

Science Objective:
Determine the emitted concentrations and total number of cloud condensation nuclei (CCN)/ice nuclei (IN)/soluble particles, concentration, and size of soot particles.

Measurement Needs:
- Measure the effects of a single contrail on radiation as a function of time from the source.
- Measure background concentrations of the same quantities, especially CCN/IN/soluble particles.
- Measure representative ice concentrations and sizes in the contrail. Determine how this result changes with temperature.
- Determine time dependence of contrail characteristics for model comparison/validation.

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Flight Profiles:
- If possible, conduct these measurements over a remote sensing site such as one of the Department of Energy Atmospheric Radiation Measurement/Clouds and Radiation Testbed (ARM/CART) sites. Ground-based lidar will be valuable for characterizing vertical extent of contrails.
- Measurements in pre-frontal conditions present highest probability of contrail formation.
- Flight altitude levels corresponding to temperatures from -35°C to -55°C (i.e., where contrail formation is likely).
- Vertical profiles, stepped soundings, and horizontal transects through contrails.

Mission 2: Determine Cirrus Nucleation Mechanisms

Science Objective:
Characterize background cloud-active aerosol population and see if there are major differences with contaminated versus relatively clear areas.

Measurement Needs
- Measure concentrations of CCN at UT altitudes, including those spanning a broader range of supersaturations than conventional because of the activation mechanisms unique to cirrus.
- Identify relevant meteorological and air mass characteristics that possibly affect these results and look for correlations between CCN concentrations and tracers.
- Measure concentrations of SO_2 and sulfate aerosols in the UT/LS to serve as input to gas-to-particle calculations and assess particle production.
- Measure IN and soluble particle concentrations and include measurements of small soot particles as possible indicators of contamination by aircraft sources.
- If possible, measure in pristine areas, (i.e., areas expected to be free of aircraft contamination).

Mission 3: Cirrus-Contrail Interactions

Science Objective:
Search for radiation effects associated with aircraft effluents from either contrail formation in clear air or contrail formation in or preceding cirrus formation.

Measurement Needs:
- Measure the optical properties of contrail particles and those of particles in adjoining or nearby cirrus. If possible, locate cirrus embedded in cirrus for comparative studies of microphysical properties.
- Measure the size distribution of ice crystals formed by contrails and compare with adjoining cirrus clouds formed in similar temperature and water vapor conditions. Use these measurements in comparing with satellite measurements and in validating inversion algorithms for optical properties and size distributions.
- Measure the chemistry and nuclei of individual ice crystals in contrails and cirrus.

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'If possible measure in pristine areas (i.e., areas expected to be free of aircraft contamination).

Mission 4: Cirrus-Contrail Interactions

Science Objective:
Search for radiation effects associated with aircraft effluents from either contrail formation in clear air or contrail formation in or preceding cirrus formation.

Measurement Needs:
- Measure the optical properties of contrail particles and those of particles in adjoining or nearby cirrus. If possible, locate contrails embedded in cirrus for comparative studies of microphysical properties.
- Measure the size distribution of ice crystals formed by contrails and compare with adjoining cirrus clouds formed in similar temperature and water vapor conditions. Use these measurements in comparing with satellite measurements and in validating inversion algorithms for optical properties and size distributions.
- Measure the chemistry and nuclei of individual ice crystals in contrails and cirrus.

All of the missions discussed are within the realm of current aircraft capabilities. The critical component in these studies is the instrumentation. The sensor technology for making the most important measurements is either inadequate or nonexistent at this time.

Clearly there are serious deficiencies in those areas critical to the mission objective, for example, the measurement of small ice crystals, which are thought to contribute significantly to the albedo of cirrus, and the scattering phase function, which is the most fundamental optical property of ice crystals. The instruments labeled "additional development needed" have either inadequate accuracies, resolutions, or time responses, and need additional development for deployment on high-altitude aircraft.

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Section 7.2

Observations - SUbsonic Aircraft: Contrail and Cloud Effects Special Study (SUCCESS) Workshop and White Paper Excerpts

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INTRODUCTION

One goal of the Subsonic Assessment (SASS) Program is to determine the impact of the current and the future subsonic aircraft fleet on Earth's radiation budget and climate. In June 1994 at the NASA Ames Research Center, a SASS planning meeting was held at which a set of specific questions related to climate and radiation was formulated (Table 7.2-1). Climate effects can occur if contrails generated by aircraft persist long enough, and occur frequently enough to cover a significant portion of the globe. They might also occur if aircraft exhaust products, such as water vapor, soot, or sulfates, build up to become radiatively significant, or if the exhaust products affect cirrus clouds which normally occur at aircraft flight levels. Finally, aircraft can affect the Earth's climate and radiation balance if they cause chemical reactions within the atmosphere which lead to changes in the concentrations of radiatively active gases such as ozone. Some of the questions outlined in Table 7.2-1 will be addressed by SASS-supported satellite remote sensing studies, laboratory studies, theoretical work, or ground-based observations. However, a number of issues require that *in situ* measurements be made. This section outlines a plan for a field program to obtain these *in situ* measurements. The acronym for this field program is SUCCESS, SUbsonic aircraft: Contrail and Cloud Effects Special Study.

Table 7.2-2 outlines SASS climate-related questions which can only be answered by *in situ* measurements. We have designed the SUCCESS field program utilizing primarily the NASA DC-8, T-39, and ER-2 aircraft to address the questions in Table 7.2-2. The DC-8 and T-39 will be used as *in situ* cloud and aircraft exhaust sampling platforms. The ER-2 will be used as a water vapor and cloud remote sensing platform, i.e., a surrogate satellite. The T-39 will be used to perform studies in the exhaust of the DC-8 itself, and to create contrails to be sampled by the DC-8. We plan to perform this field program during April and May 1996. We will base operations in Salina, Kansas, with aircraft flights concentrated in the general area of the Department of Energy's (DOE) Atmospheric Radiation Measurement (ARM) ground site in Northern Oklahoma, and with possible flights to examine wave clouds over the Colorado Rockies. The ARM site was chosen as the major location to make use of the meteorological support available at this site.

In subsequent sections of this paper we describe the rationale for the field program, the suite of instruments that will be used, and the choice of aircraft and location. We will discuss the overlap between this program, the SASS Near-Field Interactions activity, the NASA First ISCCP (International Satellite Cloud Climatology Project) Regional Experiment (FIRE), and the DOE ARM program. We will also provide sample flight plans to address specific issues.

This section was prepared as an outgrowth of the June 1994 meeting by a steering committee for the SUCCESS program, with input from the DC-8 and ER-2 mission managers and from SASS and FIRE program managers.

SCIENCE RATIONALE

In this section we will discuss the details of the science questions in Tables 7.2-1 and 7.2-2.

Contrails

The most obvious climate related issue concerning aircraft is whether or not contrails cause a significant modification of Earth's radiation budget. This issue has been considered for at least

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Table 7.2-1. Questions for subsonics program related to climate.

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1. What are the effects of contrails on the Earth's radiation budget?
   a. What fraction of the Earth is now covered by contrails?
   b. What are the meteorological and aircraft-related properties that lead to contrail formation? How do contrails and their radiative properties vary in time and space?
   c. Under what conditions do contrails develop into widespread cirrus clouds? Would these clouds have formed without aircraft, or are the aircraft responsible? Are the cirrus cloud properties different than those of clouds not affected by aircraft?
   d. Do aircraft flying through cirrus impact them either through contrail interactions or turbulence?
   e. What are the effects of the contrails on the radiative flux divergence profile, surface radiation budget, and planetary radiation balance? How do they depend on cloud properties?
   f. Does precipitation from contrails act as a significant transport process for water vapor?

2. Does aircraft exhaust affect ambient cirrus?
   a. What types of particles act as nuclei for cirrus cloud formation in the ambient atmosphere?
   b. Do aircraft emit special kinds of particles or gases that might affect ice formation?
   c. What are size and number of sulfate particles in aircraft wakes?

3. Do aircraft emit enough soot or sulfate to be radiatively significant?
   a. What is the optical depth, surface area and composition of aerosols in the upper troposphere and lower stratosphere?
   b. How much soot, sulfate, and other particles are emitted by aircraft?

4. Are heterogeneous reactions important on aircraft modified particles?
   a. Do significant heterogeneous reactions occur in aerosols, contrails or in cirrus that might affect the nitrogen oxides (NO_x) budget?
   b. What is the rate of sulfate production in aerosols, contrails, and cirrus?

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two decades [Study of Man's Impact on Climate, 1971]. Contrails that persist could be radiatively significant because they increase the Earth's albedo and diminish the emission to space of infrared radiation, like natural cirrus clouds, with possible resulting reductions or increases in the temperature at the surface. Most investigators have concluded that contrails are likely to produce a net warming at the Earth's surface, like many other high level cirrus [Liou et

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Table 7.2-2. Reasons for an aircraft flight program to study cirrus and contrails and required measurements.

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1. To ground truth satellite analyses of contrail and cirrus radiative properties.
   a. Cloud top and bottom height
   b. Cloud particle size, phase
   c. Scattering phase function
   d. Ice water content
   e. Optical depth
   f. Homogeneity
   g. Transmission, reflectance etc.

2. To investigate mode of formation of cirrus clouds/ contrails, predictability of cloud properties, persistence, spreading to form cirrus and dissipation
   a. Ice and freezing nucleus concentration/composition
   b. Cloud condensation nuclei (CCN) spectrum, condensation nuclei (CN)
   c. Aerosol size spectrum
   d. Cloud particle size spectrum
   e. Large scale cooling rate, vertical velocity
   f. Turbulence
   g. Water vapor concentration
   h. Temperature profile
   i. Aircraft tracers

3. To extend retrospective analyses of aerosol abundance and composition
   a. Aerosol composition
   b. Ice nucleus concentration
   c. CCN, CN concentration
   d. Aerosol size distribution
   e. Aerosol optical depth

4. To investigate evidence for heterogeneous chemistry on contrails or on cirrus
   a. Cycling of reactive nitrogen (NO_y)
   b. Oxidation of sulfur dioxide (SO_2)

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al., 1990]. Two-dimensional simulations by Liou *et al.* [1990] suggest a surface temperature increase of 1 K if the coverage of high clouds is increased by 5% (i.e., from 20 to 25%) from 20°N to 70°N. Hansen *et al.* [1981] found that a 2% increase in global high cloud cover would lead to a 1K temperature increase, which is about one third the response predicted by the same model for doubled CO_2. Regional scale calculations quoted in Schumann [1994], which omit several global feedback processes that were included in Liou's study [1990], suggest a linear increase in surface temperature with cloud cover due to contrails having a magnitude of about 0.05 K for a 0.4% high cloud cover increase. The somewhat different sensitivity to cloud amount in these studies may represent not only different feedbacks included in the models, but also different assumptions about the cloud optical properties.

A complete assessment of the importance of this warming effect requires adequate determination of the fraction of the Earth covered by contrails. Schumann and Wendling [1990] studied contrail coverage over Europe for one year and concluded that contrails were present about 25% of the time, but the average coverage was only about 0.4% of the area of central Europe. Liou *et al.* [1990] reported that the high cloud coverage over Salt Lake City had increased from 11.8% to 19.6% between the period 1949 to 1964 and the period 1965 to 1982, which they attribute to increased jet traffic in the second time period. Changnon [1981] and Angell [1990] both report increased high cloudiness associated with rising surface temperatures over the U.S. since about the 1960s.

Determining the aerial coverage of contrails is being done by SASS using analyses of satellite data. However, the issue is complicated by the difficulty of identifying contrails uniquely, by problems in determining the changes in radiative properties of cirrus impacted by contrails, and by ambiguity due to the spreading of contrails to form cirrus sheets. If such sheets of cirrus are common, it will be necessary to determine if they are triggered by the contrails, or if they would have formed even in the absence of contrails. Likewise, the impact of contrails on already formed cirrus is not well-understood and poses a difficult remote sensing problem. If a contrail forms in an extant cirrus layer, it may serve to stabilize the cirrus by reducing the effective cloud particle diameter. This effect results from the infusion of additional condensation and/or freezing nuclei into a cloud. These aerosols compete with the natural nuclei for the available water resulting in a cirrus cloud with more crystals having a smaller size than before. The smaller crystals have slower sedimentation rates that may effectively diminish the precipitation processes that tend to dissipate the cirrus cloud. The smaller particles also increase the albedo of the cloud with minimal effects on the infrared (IR) flux. This alteration of the Earth's radiation budget would decrease the net flux, a cooling effect. By stabilizing the cirrus layer, the contrail would cause the cirrus to last longer than usual so that the cloud's radiative effects would be extended. Aircraft and ground-based scanning lidar observations will aid in determining the degree to which contrails affect ambient cirrus.

There are also important uncertainties about the optical properties of contrails that parallel uncertainties about radiative transfer through cirrus. These uncertainties limit our present ability to make a quantitative assessment of the climatic significance of contrails. For example, Stephens *et al.* [1990] show that the radiative effects of cirrus depend sensitively upon the mean particle size and upon the scattering-phase function, in addition to the ice water content of the clouds. There are currently no *in situ* measurements of the scattering-phase functions of the

particles that compose cirrus or contrails. Measurements of ice crystal size and scattering-phase function should help answer questions about the reflectivity of ice clouds. It has been found from FIRE studies that Mie scattering calculations result in calculated cloud albedos that are lower than those observed. The error may be due either to the presence of more small ice crystals than thought to occur, or more likely to nonspherical scattering effects being greater than thought [e.g. Stackhouse and Stephens, 1991]. This lack of information not only makes it difficult to model the climatic effects of cirrus, but it also impacts the ability of remote sensors to determine the properties of contrails. There are some previous data on contrail particle sizes [Knollenberg, 1972] and some measurements of their optical properties [Kuhn, 1970]. In addition the NASA FIRE program obtained more modern data on contrail properties that is being analyzed with SASS funding. However, these data need to be updated with additional measurements such as the phase function and with more complete ice particle size distributions. In addition, remote sensing observations which attempt to derive ice water content, and particle size need to be checked against direct measurements.

Contrails represent an injection of water into the upper atmosphere. However, the majority of water in a contrail is by far from the ambient atmosphere, which in some cases exceeds the injected water by a factor of 10^4 [Knollenberg, 1972]. If a contrail develops and persists, it can provide a means for desiccating the upper troposphere through precipitation processes and for moistening lower tropospheric layers. This process can alter the absorption of IR radiation in the upper troposphere, changing the vertical profile of atmospheric cooling. In one extreme case contrails were observed to shed streamers which extended from 9 km to the ground [Konrad and Howard, 1974]. Aircraft and lidar observations of the frequency of precipitation from contrails coupled with information on the frequency of contrail formation are needed to assess the importance of this water vapor transport.

Our current knowledge regarding the magnitude of each of these various contrail effects is inadequate to assess, with any certainty, whether current and future levels of air traffic have a significant effect on global weather and climate. Although contrails themselves probably warm the Earth, their possible effects on particle sizes in other cirrus may produce cooling, as discussed above. Thus, the sign of the effect (i.e., whether contrails cool or warm the Earth's surface) is unknown at this point.

Effects of Exhaust on Cirrus

In addition to water, the exhaust from aircraft contains soot, NO_x, sulfates, and SO_2. The gaseous materials either condense within droplets in the atmosphere or are oxidized to form materials which can become aerosols. Of principal interest here is the role that these particles may play in cloud physical processes.

In the lower atmosphere it has been found that the albedo of marine stratus clouds is very sensitive to the abundance of aerosols. This effect is sometimes referred to as the Twomey effect, after the first person to suggest it [Twomey, 1977]. In water clouds, condensation occurs on all aerosol particles which are large enough and contain sufficient soluble matter to be activated. If the concentration of aerosols goes up then the number of cloud droplets is increased, and the mean size of the cloud particles is reduced. Reducing the particle size leads to

an increase in the cloud optical depth producing a brighter cloud. This effect clearly occurs in ship tracks, which are bright cloud lines formed in the particle-rich exhaust of passing ships [Coakley et al., 1987]. Empirical studies show that the exhaust from ships leads to a lowering of cloud droplet size, an increase in liquid water content, and an increase in visible albedo of the clouds [Coakley et al. 1987; Radke et al., 1989; Albrecht, 1989]. Only Ackerman et al. [1994] have tried to model ship tracks. They find that an aerosol injection into a simulated cloud leads to changes in cloud properties similar to those observed. The most surprising aspect of their simulation is that the effect of the injection on cloud albedo persists for periods of 24 hours or more, as is required to explain the length of some ship tracks.

Few studies have investigated the impact of aerosols on cirrus. Jensen and Toon [1992] found in a theoretical study that large volcanic aerosols drifting downward from the stratosphere could increase the number of cirrus cloud particles. Depending upon the height and the vertical ascent rate of the air, the cirrus contribution to the radiative budget could be modified significantly by the increased number of ice particles. Observations reported by Sassen [1992] and Sassen et al. [1995] from the FIRE program, which occurred after the Mt. Pinatubo eruption, showed that cirrus forming in air masses containing Mt. Pinatubo debris were highly unusual. Such clouds contained large numbers of particles relative to normal cirrus in a manner reminiscent of the Twomey effect. These theories and observations suggest that cirrus may respond to aerosols having properties (size or composition) that differ significantly from those of the ambient aerosols.

Jensen and Toon [1994] conducted an investigation of the sensitivity of cirrus optical properties to changes in aerosol concentrations. Only the number of particles was changed in these simulations, but the basic particle properties such as size and composition were not altered. They found that the sensitivity of the ice number density to the aerosol concentration is very slight. The model used by Jensen and Toon [1994] is essentially identical to the one used by Ackerman et al. [1994] to investigate marine stratus. Therefore, the low sensitivity to cirrus aerosols relative to stratus is not due to differences in simulation techniques, but rather to the physical processes included in the models. The cirrus model includes ice nucleation, due to the freezing of water droplets or aerosols, which occurs at substantial supersaturations with respect to ice. Once nucleation begins, the supersaturation quickly falls due to ice crystal growth, shutting off further nucleation. Thus, in this model, cirrus clouds are self-limiting in the sense that once enough particles form to control the vapor concentration, no further nucleation can occur. Stratus clouds on the other hand are more sensitive to the number of particles present because the activation and growth occur at similar supersaturations. Unfortunately, there are no observations of links between aerosol concentrations and cirrus properties that clearly tell us if these numerical simulations are correct, and no other modeling groups have performed similar simulations at present.

The formation mechanisms of cirrus clouds are not well-understood. Of the half million particles that may occupy a liter of air in the upper troposphere, only a few hundred at most will serve as nuclei for cirrus cloud formation. Current observations and theories suggest this selectivity is simply due to the freezing of sulfate particles [Sassen and Dodd, 1989; Heymsfield and Sabin, 1989; Jensen et al. 1994]. However, it cannot be excluded that cirrus sometimes, or often, form

on nuclei having some special properties. Such nuclei are called ice nuclei; many older cloud physics studies were dedicated to determining their properties.

There are a number of ways that ice nucleation and new particle formation can be categorized. Ice nuclei (IN) refer to particles on which vapor may be deposited directly in the solid form. There are also freezing nuclei which may be embedded in a soluble material and cause a liquid droplet to freeze. Cloud condensation nuclei (CCN) are particles composed of soluble material that will deliquesce at humidities with respect to water that are less than unity. They may either freeze under conditions that are supersaturated with respect to ice, but subsaturated with respect to water, or at water supersaturations. Their behavior may be a function of temperature, and of the concentration of minor dissolved species. Finally, condensation nuclei are all of the particles that will form a droplet at high supersaturation. The fraction of these that are CCN depends on the supersaturation that is reached; thus we need to know the CCN as a function of supersaturation. In order to understand how cirrus may be affected by aircraft emissions, it will be necessary to distinguish all of these nucleation possibilities and determine which is most important-a challenging task.

In order to better understand how aircraft may impact cirrus, we first must determine how cirrus nucleate. Do they form on special ice nuclei that may have an aircraft origin, such as soot? Do they form on condensation nuclei such as sulfates which may be augmented by aircraft? If they form oh sulfates, do they prefer large sulfate particles or sulfate particles that may be contaminated by soot which acts as a freezing nucleus? Are the particles pure sulfuric acid (H_2SO_4), or do they contain trace amounts of nitric acid (HNO_3) which affects their freezing properties?

Recent laboratory studies [e.g., Molina *et al.*, 1993], have indicated the complexity of H_2SO_4 aerosols in the stratosphere. Since the freezing behavior of such particles is likely to be critical to cirrus formation, the details of the particle chemistry will be essential to completely assess the role of aircraft in modifying the formation rates and eventual properties of cirrus. Laboratory studies will undoubtedly be needed. We need to know if the freezing behavior of the sulfates is affected by soot, other foreign nuclei, HNO_3, or partial ammoniation.

Of course, contrails represent one form of cirrus. Therefore better understanding of the mechanisms of contrail formation will aid in the understanding of the role of aircraft debris in impacting cirrus.

Radiative Properties of Exhaust

The soot and sulfate emitted by aircraft will contribute to the burden of aerosols in the upper troposphere and lower stratosphere (UT/LS). It is possible that the resulting aerosol optical depths, which are roughly proportional to the aerosol surface area, could be radiatively significant. However, neither the nonvolcanic stratospheric optical depth, nor the upper troposphere aerosol optical depth is currently climatically significant. Despite its probable lack of importance, a complete assessment of aircraft effects will require that the direct radiative effect (i.e., those that do not involve clouds) of aircraft-generated aerosols be quantified. The possibility of heterogeneous chemistry on the aerosols must also be assessed. It is known that

the background stratospheric aerosols have enough surface area to significantly perturb the nitrogen chemistry of the stratosphere. These perturbations are directly relevant to stratospheric aircraft.

SASS is addressing the properties of aircraft-generated aerosols in the UT/LS primarily through retrospective analyses. A short aircraft campaign cannot obtain enough information to be climatologically important; however, a number of issues can be addressed that previous data sets may not have fully covered. For example, the composition of the aerosols in the upper troposphere has not been measured in detail except on a few missions. The aerosol radiative properties depend on composition.

Heterogeneous Chemistry on Contrails and Clouds

Chemical reactions occurring within aerosol particles or on the surface of these particles are known to play a critical role in modifying the composition, hygroscopicity, and size distribution of the atmospheric aerosol. These reactions may also significantly affect ozone levels in the UT/LS by acting as sources and sinks of radicals, particularly NO_x. Our current understanding of aerosol chemistry in the UT/LS is very poor and needs to be considerably improved if perturbations from aircraft are to be reliably assessed. SUCCESS offers an excellent opportunity to begin such studies. The detailed characterization of aerosol and ice particles to be made onboard the DC-8 can be complemented with a minimum package of gas-phase chemical instrumentation to allow major advances in our understanding of aerosol chemistry. Such gas-phase instrumentation is needed to help identify aircraft exhaust even if it were not our goal to study heterogeneous chemistry. The heterogeneous chemistry component of the SUCCESS mission will focus on preliminary steps toward addressing the chemistry questions outlined in Tables 7.2-1 and 7.2-2.

Recent aircraft measurements in the upper troposphere indicate that the NO_x/HNO_3 concentration ratio is much higher than would be expected from known gas-phase photochemical equilibrium, implying a missing source for NO_x [Chatfield, 1994]. These measurements also indicate that a large fraction of NO_y often cannot be accounted for by NO_x, HNO_3, or peroxyacetyl nitrate (PAN), possibly implying a major contribution to NO_y from an unknown species [Sandholm et al., 1992]. It has been hypothesized that uptake of HNO_3 by aerosols, followed by subsequent reaction of HNO_3 within the aerosols, could explain both the missing source of NO_x and the NO_y shortfall. However, there is no experimental evidence to test this hypothesis, and there is little knowledge of the possible aerosol mechanisms involved. Recent measurements in the Second Airborne Arctic Stratospheric Experiment (AASE II) indicate a sharp rise of the NO_x/NO_y ratio during passage through cirrus, suggesting that reactions in cirrus might be important in chemically regenerating NO_x. SUCCESS can improve considerably our understanding of the role of aerosol chemistry in the NO_x budget by concurrent measurements of aerosol characteristics and of the gas-phase concentrations of NO_x, HNO_3, and NO_y.

Gas-phase oxidation of SO_2 to sulfate in the upper troposphere is thought to represent a major, and perhaps dominant, source of new particles to the troposphere. However, the role of heterogeneous SO_2 oxidation in moderating this new particle formation is not understood. There is laboratory evidence that rapid oxidation of SO_2 takes place at the surface of soot and other

aerosol particles [Brodzinsky *et al.*, 1980], but the importance of these reactions as sinks for SO_2 in the atmosphere has yet to be documented. Heterogeneous oxidation of SO_2 complicates the assessment of the effect of aircraft on new sulfate particle formation. Aircraft could increase nucleation due to emission of SO_2, but could also suppress nucleation due to direct emission of soot and other particles (providing sites for heterogeneous SO_2 oxidation). The SASS mission can provide a first assessment of this issue by concurrent measurements of aerosol characteristics, SO_2, and sulfate over a range of conditions.

INTERACTION WITH THE SASS NEAR-FIELD PROGRAM

In addition to the climate-related issues described above, SASS also has questions related to emissions close to the aircraft, which is referred to as the near-field. Since a number of near-field questions can also be dealt with using the same instrument package that is required to address climate issues, we describe here some near-field objectives for the SUCCESS mission.

Table 7.2-3 outlines some of the principal.questions related to the near-field portion of SASS. Many of these questions closely parallel or overlap those discussed previously for climate. The major new issues have to do with the dynamics of the exhaust plume behind an aircraft, the emission indices of aircraft engines, and questions about sulfate particle formation in an exhaust trail.

Numerical models of exhaust trail formation have been constructed [e.g., Miake-Lye *et al.*, 1993]. These suggest that the engine exhaust is quickly entrained into the vortices generated by the wings of the aircraft. These vortices dominate the transport and spreading of the exhaust material for a short period of time. Due to the turbulence in these vortices, it is difficult to fly close behind another aircraft. Therefore the vortices represent an impediment to making good measurements. There are few data to determine the degree to which the engine exhaust is actually entrained in the vortices so observations of this phenomena would be desirable. Fortunately, some information about the entrainment of exhaust into the vortices may be obtained using a scanning lidar which does not require flying inside the vortices.

The emission indices (EIs) for various materials can be determined by measuring the ratio of the material in question to the concentration of carbon dioxide. Carbon dioxide (CO_2) is used to normalize for the dispersion of the plume.

Measurements in the distant wake can also be useful to infer chemistry in the near field that may be difficult to observe directly. For example, the hydroxyl radical (OH) drives most of the chemistry within and near the engines, but it disappears so rapidly that *in situ* measurements are impractical. However, measurements of the nitrous acid (HONO)/OH/NO_y ratios well behind the aircraft can be used to estimate OH levels at the engine exit. Similarly measurements of the ratios of HNO_3/NO_x can be revealing.

SO_2 is only partially oxidized in the near field [Schumann, 1994]. However, that which is converted to H_2SO_4 is thought to form the nuclei on which contrails form. It would be advantageous to measure both SO_2 and H_2SO_4 so that theories of this transformation could be checked [Miake-Lye *et al.*, 1993].

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SASS is currently equipping a NASA T-39 aircraft, a small jet aircraft similar to the National Center for Atmospheric Research's (NCAR) former Sabreliner, for near-field studies. This aircraft will be used in conjunction with the DC-8 and ER-2 in the SUCCESS program to improve the near-field measurements.

Table 7.2-3. Questions related to the near field.

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1. Are current models adequate for predicting the interactions between the exhaust from the engines and the flows generated by the airframe?

2. What are the emission indices in flight for NO_x, SO_x, and soot?

3. How much of the emitted gaseous SO_x is converted to particles near the aircraft? What are the properties of these sulfate particles? How do the sulfate particles interact with soot particles?

4. Do contrails form on the sulfate particles in the exhaust or on the soot particles in the exhaust? Are contrails sensitive to the amount of sulfate in the exhaust? To what degree are exhaust particles CCN, IN, or just CN.

5. How much of the emitted NO_x is oxidized in the near field? What are the products of the NO_x oxidation?

INTERACTION WITH FIRE

There are other NASA and other agency programs that have a close overlap with the interests of SASS. We plan to interact with these programs to extend the kinds of problems that can be considered.

The NASA FIRE program has already conducted two major cirrus-related field programs. FIRE conducted its most recent cirrus study in the general vicinity of the current ARM ground site where we propose to conduct SUCCESS. Some data from the most recent FIRE program are being analyzed with SASS funding because they pertain directly to SASS issues. For instance, one FIRE aircraft crossed its contrail several times and obtained valuable microphysical data. In addition the NASA ER-2 observed contrails in cirrus with remote sensing data during FIRE. These data clearly show that contrails differ radiatively from the surrounding cirrus.

During the SUCCESS field activity we will interact with a small-scale FIRE campaign involving the ER-2 instrumented in a manner similar to that of previous FIRE missions. A possible ER-2

payload is described below. Many of the SUCCESS goals are directly relevant to those of FIRE, so there is a strong overlap. The mechanisms for ice crystal nucleation and aerosol effects are a high priority for FIRE as well as SASS. In addition, FIRE has identified a number of open issues, such as the importance of small particles and the importance of the scattering-phase function to the cloud reflectivity, which the SASS-instrumented DC-8 should be able to help resolve.

STRAWMAN DC-8 PAYLOAD

The DC-8 aircraft has been selected as the primary SASS-funded aircraft to investigate the importance of subsonic aircraft to climate and radiation issues. The primary reasons for selecting the DC-8 are its large instrument payload capacity, its ability to reach altitudes frequented by commercial air traffic, and its ability to reach altitudes where many cirrus are located. Of course, the DC-8 has some liabilities. Due to the large size of the aircraft, sampling ports can be separated by 10 meters or so, making it difficult to correlate measurements in a highly heterogeneous environment such as an aircraft wake. The DC-8 will not be able to reach some cirrus clouds or cirrus cloud tops which extend above ~11 km. In addition, many measurements will require the use of two or more aircraft. For instance, the DC-8 takes about eight minutes to complete a circle and sample its own exhaust. Therefore, near-field problems requiring closer sampling will need another aircraft to create a wake for the DC-8, or to sample the wake of the DC-8. For this reason, we will use the Langley T-39 for additional near-field sampling. As another example, it is difficult to coordinate passes of satellites with aircraft observations. Therefore, we plan use the ER-2 equipped with relevant radiometers as part of the mini-FIRE campaign to act as a surrogate satellite. We will discuss the use of the ER-2 further below.

Table 7.2-4 delineates the strawman DC-8 payload to address the issues discussed previously. Table 7.2-4 also indicates which questions in Table 7.2-2 the instruments address. All of the instruments listed in Table 7.2-4 represent a strawman instrument compliment. All of the payload may not fit on the DC-8 when details of all the instruments are known, and useful instruments may be found that were not considered in the strawman payload.

STRAWMAN ER-2 PAYLOAD

We plan to employ the ER-2 as a remote sensing platform, much as it has been used in previous FIRE programs. Essentially, the aircraft will be used as a surrogate satellite. A possible ER-2 FIRE payload is described in Table 7.2-5. Two sorts of instruments are suggested for the aircraft payload. First, a water vapor lidar would provide vertical profiles of water vapor in the troposphere. These data will compliment the DC-8 *in situ* measurements and will be used to understand the conditions leading to the formation of cirrus and contrails. The lidar will also be used to detect cirrus clouds and to measure the altitudes of cloud top and bottom (for optically thin clouds). The second type of instrument includes high-resolution visible and IR spectrometers. They serve as surrogates for satellite data so that the ability to retrieve particle size or cloud optical depth from satellite remote sensing can be ground-truthed. In addition, an imaging spectrometer system will see a much larger field of view than the DC-8 occupies. Therefore, the imaging system will help put the DC-8 observations into the context of the cloud

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field being studied. Finally, broad-band net-flux radiometers on the ER-2 will be used to evaluate the radiative signatures of cirrus and contrails.

MISSION SCHEDULE, SITE SELECTION, AND INTERACTION WITH ARM

We currently plan to conduct SUCCESS during April and May 1996. Aircraft flights will be concentrated in the general area of the ARM field site in northern Oklahoma and Kansas, with excursions to the Rocky Mountains near Boulder, Colorado to study wave clouds. The aircraft, science investigators, and mission operations will be conducted from Salina, Kansas, a location compatible with ER-2 operations.

We plan to load the SUCCESS mission instruments on the DC-8 beginning in late February 1996, with test flights completed by mid- to late March so that deployment can occur in April and May 1996. These dates were chosen to be compatible with other projects on the DC-8 payload schedule, to finish the project within FY96, and to perform the study at a time of year when cirrus clouds are likely to be found easily. In addition, we wish to avoid winter flights in order to make it easier to operate the ER-2 aircraft, which cannot land on icy runways. The mission duration is determined by the number of flights planned as discussed below.

Table 7.2-4. Strawman DC-8 payload.

Instrument	Questions addressed
Aerosol composition	3a, 2a, N2, N3
Aerosol size	2c, 3d, N3
CN number/volatility	2b, 3c, N2, N3
CCN versus Supersaturation	2b, 3c, N2, N3, N4
Ice particle size	1bf, 2d
Ice particle scattering phase function	1cf
Ice water content	1df
Ice nuclei composition	2a, 1f, N2, N3, N4
Ice nuclei concentration	2a, 3b, N2, N3, N4
Temperature, winds, turbulence	2hf, N1
Temperature profile	2h, N1
Scanning Lidar	1af, N1
Water vapor	2g
NO_x, NO_y, HNO_3, other nitrogen species	2i, 4ac, N2, N5
Tracers (CO, CO_2, CH_4, N_2O, etc.)	2i
H_2SO_4, SO_2	4b, N2, N3
Net flux solar and IR radiometers	1g

Table 7.2-5. Strawman ER-2 payload.

Water vapor lidar	2g
Cloud lidar	1a
High-spectral-resolution visible/IR radiometers	1g
Imaging spectrometers	1g
Net flux solar and IR radiometers	1g
Microwave radiometer	1d, f

Based upon surface reports of high cloudiness, cirrus frequencies peak in the winter months [Warren et al., 1986]. However, in the area of Kansas and Oklahoma, cirrus are only slightly less abundant in March to May than they are in the winter. During these spring months, cirrus clouds are observed 68% of the time over the Oklahoma-Kansas area, while they are present only about 37% of the time in the area of the NASA Ames Research Center, Moffett Field, California. During June to August, cirrus frequencies are still high over the ARM site averaging about 62%.

The DOE ARM program has established a ground site in northern Oklahoma and has begun a program of atmospheric measurements of the radiation field using unmanned aerial vehicles (UAVs). We have chosen the ARM site as the central point of the SUCCESS field program for several reasons. First, the previous FIRE program and the DOE aircraft programs have led to a lot of experience with aircraft operations at cirrus altitudes at this location. Aircraft logistics will be a major difficulty in SUCCESS, so having an established air traffic control relationship with be valuable. In addition, the ARM site has a large number of useful ground-based instruments, some of which (e.g., the all-sky cameras) are being used by SASS investigators to study contrails. The ARM site also can serve as a useful location for some SASS-funded ground-based instruments such as scanning lidars. However, it should be noted that the airspace directly above the ARM site is largely controlled by military airspace restrictions. If this airspace cannot be used, then most of the flights will have to occur away from the central site. Although the meteorological support from the ARM site would still be of value, the ground-based instruments there would be less useful.

The suite of ARM instruments has been described by Stokes and Schwartz [1994]. The principal goal of the ARM program is to better constrain the radiation budget, so there are numerous radiometers at the site, as well as various profilers and sondes to measure atmospheric state parameters. In the case of an intensive program like SUCCESS, it is likely that additional instruments will be used at the ARM site by ARM investigators, such as water vapor lidars, light aircraft instrumented to study radiation, and so forth.

Although the ARM site will be favored as a locale for measurements, some aircraft flights may occur in other regions if favorable conditions do not occur at the ARM site or if interesting conditions occur elsewhere.

In order to achieve a coherent scientific program, we plan to locate the DC-8, ER-2, and science investigators at the same airfield in Salina, KS, and to use this airfield as the actual operations base. The Salina airfield offers the special facilities required to operate the ER-2 aircraft.

STRAWMAN FLIGHT PLANS AND MEASUREMENT STRATEGY

Here we describe some typical flights that might be made during the SUCCESS mission. Actual flights will depend upon the local meteorology, aircraft availability, and other practical considerations. We plan to develop a more thorough flight plan strategy after the instruments have been selected. We discuss these flights below in sections which correlate with particular meteorological situations. We also relate these flights to the questions in Tables 7.2-2 and 7.2-3 to which they provide answers. In total, these flights and test flights would require about 126 hours of DC-8 flight time, and similar amounts of time on the ER-2 and T-39. To conduct this number of flights would require about four weeks, assuming that flights were made at every opportunity. We assume that the actual duration of the project, not including instrument integration, will be about six to seven weeks, with one to two weeks at Ames and the remainder in the field.

Because we have a large number of questions that we wish to address, it is necessary to have a priority listing of which questions we will address first. These priorities will change as data are obtained. In general, our first priority will be to investigate contrails and cirrus clouds over the ARM CART site. Our second priority will be to study wave clouds over the Rocky Mountains. Our third priority will be to investigate the properties of cirrus clouds over the Gulf of Mexico. These priorities reflect the order in which meteorological data will be studied in flight planning. We expect to conduct all of these studies at some time during the mission. We also have a lower priority set of missions that will be conducted if none of the higher priority flights can be done on a given day because of adverse meteorology. These secondary mission goals include studies of the aerosols in the outflow from convective clouds, investigations of the variations in atmospheric chemistry during sunrise and sunset, and studies of aerosols and radiation fields in clear skies. It is likely that we also will conduct most of these missions at some time during the SUCCESS campaign since there is a high likelihood of extended periods of either clear skies or convective activity during the deployment.

Near-Field Studies of Exhaust without Contrails

These investigations are aimed at characterizing the emissions from various aircraft. Two issues are most important. First, we need to determine the EIs, and verify chemical models in the aircraft wake. This issue depends on aircraft engines and fuel characteristics. Second, we would like to verify the dynamics in the wakes behind multi-engine aircraft. This issue depends upon the type of aircraft involved, rather than the engines and fuel. In either case we would like to use NASA or other dedicated aircraft whose characteristics are known. Prior to flight, a sample of the aircraft fuel will be obtained. We propose that most of these flights be conducted from

NASA Ames during the test flight series for the DC-8. NASA aircraft that might be studied include the C-141 based at Ames, as well as various aircraft based at NASA Dryden. A selection of which aircraft should be studied will be done in collaboration with the near-field study portions of SASS.

A typical flight profile might be done as follows. An aircraft is selected and its fuel is sampled before flight. The DC-8 flies just beneath the other aircraft and moves side-to-side across the exhaust trail of the other aircraft using a scanning lidar to paint an image of the exhaust plume. The microwave temperature profiler would also be used to look at the thermal anomalies in the exhaust trail. The DC-8 then increases its distance behind the other aircraft until the exhaust trail is no longer recognizable against the background. These data should help to determine if dynamical models of the interaction of the vortices and the engine exhaust are correct. At that point, the DC-8 would ascend into the exhaust trail using the scanning lidar to locate the trail. Again the DC-8 would slip back and forth across the trail to sample the variations in the trail. The DC-8 would then move forward toward the other aircraft until the turbulence encountered became significant. During this maneuver, CO, CO_2, and other tracers would be used as aircraft exhaust identifiers. Scanning lidar observations would locate the DC-8 within the wake of the other aircraft. Turbulence characteristics, water vapor, particle properties, H_2SO_4 vapor, NO_x, and NO_y would be measured. These data would determine the EIs and also check chemical plume theories. Another map of the interactions of the aircraft vortices and exhaust would be obtained as the DC-8 advances, continuing up to the engine exit plane by having the DC-8 approach the aircraft below the region which is turbulent. The total flight time required to perform these observations should not be more than a few hours, so several aircraft plumes could be mapped in this way. We suggest that this process be repeated on separate flights to allow for the possibility of instrument failure and to allow for alternative flight strategies if interesting issues develop.

In addition to other aircraft, the DC-8 will be flown into its own exhaust. Of course, one cannot approach more closely than about eight minutes into the DC-8 exhaust due to the time required to turn the aircraft. Therefore, the main goal of this work will be to characterize the DC-8 exhaust which is of value because the engines on the DC-8 are in wide use by the commercial fleet.

These flights will address issues 3 and 4 of Table 7.2-2 and questions 1, 2, and 3 of Table 7.2-3.

If we assume that two six-hour test flights are conducted, and that two more six-hour flights are used for these emission characterizations, then this portion of the SUCCESS program would require about 24 flight hours for the DC-8 and the T-39 if it fully participates. The T-39 has a limited flight duration and may not be able to fully participate in each flight. Test flights also would be needed for the ER-2 and T-39, potentially consuming ~12 flight hours for each of these aircraft.

Contrails Not Embedded in Cirrus

The near-field program and the radiative effects program address basically the same issues with respect to contrails. In this section we consider contrails that are not embedded in cirrus clouds.

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These studies should be conducted using the DC-8, the ER-2, and another aircraft. To be specific, we assume here that the other aircraft is the T-39 and that it contains particle-sampling instruments. The issues to be studied here involve the meteorological circumstances needed to produce contrails, the meteorological circumstances needed to produce persistent contrails, the effects of aircraft fuels on contrails, the microphysical properties of contrail particles, and the radiative properties of contrails.

The meteorological circumstance needed to produce contrails will be investigated by flying the DC-8 and T-39 in the general vicinity of the ARM site during the time when a front is approaching. It is commonly observed that contrails form in particular altitude regions under these conditions and that their persistence varies with time and altitude. The first part of the observations, which might consume 1.5 hours of flight time, would be to fly 3 sets of 20-minute straight legs with the two aircraft in roughly parallel flight, but displaced vertically by a kilometer. The three sets of legs would be offset by 2 km to the maximum altitude of the aircraft. Thus, about 6 km of altitude would be covered with 1-km resolution. The ER-2 would fly at high altitude along the same general flight track in order to map out water vapor and to observe the contrails. The flight tracks would be made slightly upwind of the ARM ground lidars so that portions of the contrails would advect over the ARM lidars. By observing the contrail produced by the aircraft from whole sky cameras on the ground and from imagers on the ER-2, correlations can be drawn between the observed contrail properties and the meteorology. The meteorology would be determined using the water vapor profiler on the ER-2, the instruments at the ARM site, and *in situ* instruments on the DC-8 and T-39. The two aircraft would then return to the altitude at which the most persistent contrails were found, and the DC-8 would be used to follow the T-39 in its contrail to determine the particle properties which give rise to the radiometric observations on the ER-2. Then the aircraft would reverse position and the T-39 would follow the DC-8. The DC-8 would make a series of short vertical ascents through different portions of the T-39 contrail in order to determine the vertical variations of radiative flux through the clouds. These observations would require about two hours of flight time. If the contrail were sufficiently persistent, then the DC-8 would turn and sample it own contrail. These maneuvers would probably require another half hour of flight time. The series of observations in which the two aircraft follow each other would be repeated for contrails with different amounts of persistence.

It would be desirable to repeat these observations using fuel with a widely varying sulfur content. Preferably one aircraft would use fuel without sulfur; however, the DC-8 engines cannot use no-sulfur fuels.

These flights should address questions 1, 2, and 4 of Table 7.2-2 and questions 4 and 5 of Table 7.2-3. In addition, question 3 of Table 7.2-2 will be addressed during the contrail-free portions of the flights.

Assuming that these contrail observations are done four times, once with varying sulfur content in the fuel and three times to make certain that a variety of meteorological conditions are sampled, it would consume about 32 hours of flight time including transits between the ARM site and Kansas for the DC-8, ER-2, and T-39. It also would be desirable to fly one night flight to determine the NO_x/NO_y ratio in a contrail after dark. This mission would be flown using only

the DC-8 and might require an additional six flight hours to insure that a persistent contrail could be made and sampled. Performing these flights will require that air traffic control allow our aircraft complete use of the air space over the ARM site for most of the day.

Flights in Cirrus

There are a number of reasons for SASS to investigate cirrus properties. First, we need to determine the influence that contrails may have on cirrus. The radiative properties of contrails within cirrus, and the radiative properties of cirrus modified by contrails, may be quite different than the radiative properties of ambient cirrus or those of contrails in cloud-free regions. Second, we need to determine if aircraft exhaust products are affecting cirrus clouds. Third, we need to have a good understanding of cirrus radiative properties and cirrus formation mechanisms so that we can extrapolate any information about exhaust affecting cirrus to the global scale.

In these flights the DC-8 would be used to obtain detailed microphysical and chemical information in the clouds, the T-39 would obtain microphysical profiles through the clouds, while the ER-2 observes the radiative properties from aloft. The DC-8 would also be used both to create a contrail within a cloud as well as to sample any persistent contrails it was able to make or that were made by the T-39.

A number of issues would be addressed in these flights. For example, direct sampling of cirrus ice particles and analysis of the nuclei within them will help determine the types of nuclei on which the clouds form. In addition, determining the abundance of IN in the atmosphere around the clouds, as well as comparing the size distributions of aerosols within and outside the clouds may provide additional clues about nucleation mechanisms. Comparing the size distributions of ice crystals in contrails with those in cirrus may also reveal information about particle nucleation mechanisms. It would be particularly interesting to locate air which originated from an aircraft and had been incorporated within a cirrus after contrails had dissipated. Such samples might directly reveal if aircraft-enhanced aerosol levels had an impact on the radiative properties of the aerosols. Unfortunately, it is not obvious how to identify such aircraft exhaust in most cases. Clearly, contrails embedded in cirrus would be of increased importance if it can be shown that they alter the properties of the cirrus as they expand.

We envision 32 hours of flights dedicated to cirrus clouds for the T-39, ER-2, and DC-8. These flights would be located over the ARM site to maximize the meteorological and radiative observations of the clouds.

As mentioned above, it would be of great interest to perform a well-designed experiment to expose a cirrus cloud to aircraft exhaust. A natural possibility would be to use a lenticular cloud. In this case the ER-2 would remain stationed above the lenticular cloud to determine if the radiative properties of the cloud were modified by the exhaust. The DC-8 would first fly from downwind to upwind through the cloud to sample the ambient properties of the cloud. The DC-8 would then fly upwind of the cloud to concentrate aircraft exhaust in the cloud. Finally, the aircraft would fly back through the cloud to determine the modified properties of the cloud. There are several difficulties in performing such an experiment. The only likely locations for such lenticular clouds are the Rocky Mountains, which are far removed from the Texas base of

operations. Second, accurate predictions for the formation of ice clouds in lee waves would be needed. Such clouds would also have to fall within the altitude domain of the DC-8. It would be interesting to use both the DC-8 and T-39 to determine if the altitude of the waves clouds has any impact on the influence of the jet exhaust. This sort of experiment would be a prime demonstration of the influence, or lack of influence, of aircraft on clouds. Therefore, we plan to more carefully determine its feasibility. If possible, we will dedicate two flights, or about 16 flight hours, for the DC-8, ER-2, and T-39 to perform this experiment.

The flights discussed in this section would address questions 1, 2, and 4 in Table 7.2-2.

Clear Sky, Convective, and Stratus Cloud Flights

Some time would be spent in clear sky on many of the previously discussed flights. These data will be important for determining the natural abundance of CCN, CN, and IN in the upper troposphere. If it is clear that air masses with different origins have not been sampled adequately during the other flights, then special flights should be made. For instance, tropical air masses are within easy reach of Texas, and in April polar air also should be available. Moreover, air which has recently been lofted by convection might contain aerosols with differing composition from either boundary-layer air or air which has resided in the upper troposphere for some time. Contrails are frequently observed near convective clouds, so such air masses should be investigated to determine their aerosol properties.

Although cirrus clouds are the most frequent type of clouds at aircraft cruise altitudes, there are also stratus clouds which are encountered either on takeoff or on short duration flights. We will conduct at least one flight through stratus clouds. There will be several goals to this flight. One will be to measure the radiation field in the stratus deck, as well as above the stratus, in conjunction with *in situ* microphysical data to test the ability of radiative transfer codes to simulate clouds. Stratus clouds are much more horizontally uniform than cirrus, and so it should be much easier to calculate their optical properties than it is for patchy cirrus. In addition we will use the DC-8 to fly through the stratus to determine the effects of jet aircraft on the clouds. It is known that propeller-driven aircraft sometime produce ice crystals in supercooled clouds [Rango and Hobbs, 1983; Woodley *et al.*, 1991]. Aircraft exhaust should act as nuclei for stratus clouds that are at temperatures above freezing, leading to more and smaller particles. However, aircraft flying in supercooled clouds might produce ice crystals which would lead to an increase in particle size via vapor transfer to the ice.

We will plan at least two flights to investigate the environments in stratus clouds, convective clouds, or clear sky. We estimate that about 16 hours of flight time will be used for this purpose.

These flights are aimed at questions 1 through 4 in Table 7.2-2, with emphasis on other types of clouds than cirrus.

OPERATIONS MANAGEMENT PLAN

The SUCCESS program will be a complex field mission involving multiple aircraft, a large number of investigators, and several funding agencies. One of the project goals is to coordinate the aircraft flights so that the maximum synergy is obtained. In order to insure that the project has the maximum science return, we plan to implement the following management structure:

Project Scientist: The Project Scientist will have the overall responsibility to ensure that the goals of SASS, FIRE, and other elements of the program are met during the field program. The Project Scientist will act to coordinate and organize science team meetings in the field, as well as before and after the mission. The Project Scientist will maintain science oversight of the project in the field to insure that aircraft flights are coordinated and aimed at relevant issues. Together with the Mission Scientist, the Project Scientist will make final decisions about the flight plans for each flight series. The Project Scientist will resolve conflicts that may arise over data protocols or other issues.

Mission Scientist: The Mission Scientist will design the general flight plans for all of the aircraft. The Mission Scientist will manage the meteorology team and the air traffic control liaison, and will be responsible for conducting the flight planning meetings. The Mission Scientist will determine what is practical to accomplish on a given day considering the meteorological forecasts, aircraft availability, and air traffic control limitations. Together with the Project Scientist, the Mission Scientist will make final decisions about the flight plans for each flight series.

Project Manager: The Project Manager will be responsible for setting up the science facilities in the field including hotels, lab space, Internet connections, and so forth. The Project Manager will establish the data archiving protocol to be used and will assist investigators so that they adhere to the data archiving protocol.

Aircraft Flight Scientists: Each aircraft will have a Flight Scientist. The Flight Scientist will be responsible for acting as a spokesperson for the Principal Investigators (PIs) on their respective aircraft and for finalizing the detailed flight plans with their air crews. It is vital that the Flight Scientists agree to allow the Mission Scientist to determine the general flight plans so that aircraft coordination can be maximized.

Meteorology Team: A small group of meteorologists will be established to forecast contrail and cirrus locations during the mission so that flight planning can be done.

Air Traffic Control Liaison: An experienced air traffic control liaison will be established to communicate with the air traffic control system near the ARM site.

Instrument PIs: The instrument PIs will have full responsibility for their instruments, for keeping their co-investigators informed of all details of the project, and for delivering data to the archive in a timely fashion. The PIs will control their data to the extent that no one else can publish it without their consent and inclusion as a co-author if desired, during a fixed period of time after the mission.

Theory Team: A small theory team will accompany the SUCCESS mission in the field. The role of the theory team will be to provide advice about flight planning; to perform real-time analysis of data products to ensure that science questions are being resolved; and to interact with experimental PIs, as determined by the data protocol, to coordinate analysis of data sets from different PI groups.

DATA MANAGEMENT PLAN

It is absolutely essential that data obtained during the SUCCESS mission be archived and made available in a timely fashion. Because SASS is an assessment program, the data need to be made available to perform the assessment. It is very difficult to analyze datasets from which crucial information may be missing. Moreover, it is clear from previous field programs that data which are not made available either in real time, or within a short interval following the experiment, have little impact on the conclusions that are drawn. In short, data delivered long after the mission may as well never have been taken.

Other elements of the Atmospheric Effects of Aviation Project (AEAP) which use the ER-2 chemistry package have a data protocol which calls for data delivery within a few hours of aircraft landing. This protocol has been established over many years and has led to a very successful interaction between data collection, mission planning, and data analysis. However, there are several reasons why such a protocol cannot be expected for SUCCESS. Investigators actually fly on the DC-8 so they do not have the ability to prepare for data analysis while the aircraft is in flight. Many of the instruments have a much more complex data stream than the one-dimensional variable versus time framework of the ER-2 chemistry payloads. The DC-8 instruments discussed here do not have the long history of flying together which have allowed the data exchange format as formalized for the ER-2. Nevertheless, SUCCESS must make every attempt to have rapid data dissemination and archiving.

Our data plans call for every instrument to produce some data product, either in real time or within a day of landing. To the extent possible these data products will be archived, although some products such as photographs may not lend themselves to archiving in digital form. These products will be used for flight planning and for real-time data analysis. In addition, each data team will be required to produce an archivable data product within six months of the end of the mission, at which time a follow-up mission meeting will occur. These products will allow the project to schedule a submission date to a special issue of a journal such as *Geophysical Research Letters* within one year of the end of the mission.

A data protocol will be developed by the instrument team PIs so that proper credit will be given for shared data. The ER-2 polar campaigns have had very effective data protocols which both encouraged the dissemination of data and its analysis by theory teams, while protecting the rights of instrument PIs to be acknowledged for their hard work in obtaining the data. It has been found that everyone benefits when datasets are made available in a timely fashion and are coordinated.

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Section 7.3

Report on Commercial Platforms

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Retired, Aeronomy Laboratory
National Oceanic and Atmospheric Administration

Attempts to represent the relatively large variability inherent in tropospheric transport requires acquisition of an extensive spatial and temporal observational database of relevant chemical tracers. Both satellite-based measurements, which are beyond the resources of the Subsonic Assessment (SASS) Program, and large-scale airliner-based measurements hold the potential for such "climatological" characterizations. An ad-hoc panel meeting was held on 23 February 1994 in Washington, DC to consider the possible application of commercial or military subsonic aircraft as platforms for climatology measurements. The meeting was chaired by A. Schmeltekopf (National Oceanic and Atmospheric Administration (NOAA), retired), and attended by a number of members of the atmospheric and aeronautical communities, in particular D. Fahey (NOAA), N. Krull (Federal Aviation Administration), D. Peterson (Jet Propulsion Laboratory/NASA Headquarters), M. Prather (University of California, Irvine), B. Ridley (National Center for Atmospheric Research), R. Rood (NASA Goddard Space Flight Center (GSFC)), R. Stolarski (NASA GSFC), A. Thompson (SASS Project Scientist), H. Wesoky (SASS Project Manager), and K. Wolfe (Computer Sciences Corporation).

The specific goals of the meeting were to answer the question: Are there any experiments that can be conducted using a subset of the commercial or military subsonic fleet as a platform that would test essential elements of general circulation models? Of particular interest is the dynamics of the atmosphere near the tropopause. For NASA purposes, the question is: Can one model with confidence the dynamical fate of subsonic and supersonic aircraft emissions and, if not, what measurements can one make that would lead to improvements to or increased confidence in the models?

The group agreed on the importance of avoiding some of the lessons learned from the Global Atmospheric Sampling Program (GASP) [Hogan and Mohnen, 1979; Jasperson et al., 1985] It seemed most likely that those lessons resulted from the fact that there were no users who were part of the program planning and no users who had pledged to use the data promptly. As a result, the quality of the data was not tested by the user community until it was too late to make improvements. In addition, the dataset has received low marks from the experimental community. Thus, the dataset has been virtually unused to test or improve models.

In order to insure that there was sufficient interest in the modeling community for data of this type, at least half of the invited participants at the February 1994 meeting were active atmospheric modelers. The fundamental question issued to them was: If a climatological data set is obtained for a particular species, would they use it? Unless the answer was an enthusiastic yes, the experiment was rejected as a possibility. From the experimental side, the group recommended the use of instruments that had a reliable history; ones that had an easy, reliable calibration method; and ones that were capable of operating for extended periods without maintenance.

There are two user communities for the data: those that can assimilate the data and therefore can use data taken at almost any time and place, and those that require monthly or seasonal means to compare with model results. In order to satisfy the latter community, we must design experiments that will be flown on fairly regular routes and for a minimum of several years.

The types of experiments that were discussed fell into three groups: 1) those for which the data were being taken on aircraft presently in operation but the data either were not recorded or were not available to the scientific community, 2) those for which slightly modified aircraft equipment would be capable of taking the data, and 3) those that require installation of new, potentially complex scientific instruments on selected aircraft.

One experiment that should be continued involves obtaining the high-resolution measurements of wind, location, and temperature that are regularly made on modern aircraft. Normally the tapes are just written over and the data lost. The initial data that were obtained showed, for southeast Asia, a disagreement with the model calculations of 10 to 15% in wind velocity and a rather substantial mislocation of the jet axis. J. Tenenbaum (State University of New York, Purchase) has proposed to continue these studies for some few airline routes. Additional data, particularly in the Pacific and virtually any part of the Southern Hemisphere, would be valuable. The reason the initial studies were made in southeast Asia is because the area has such unique land-ocean morphology and such strong interaction with the Himalayan Mountains and, since there is so little data from that area, the models are likely to be in error there. It was recommended that a suitable proposal for obtaining wind velocity data from commercial airliners be funded and, if it seems warranted, to expand such a study by asking the airlines themselves to supply the data to the community.

It has been suggested that the subsonic fleet has an impact on global climate through the production of contrails or thin cirrus. We know little about the production of thin cirrus by aircraft and even less about the relative importance of that production to the natural production. It has been shown that one can use a commercial aircraft weather radar to detect cirrus particles and it is possible that a large body of relevant data could be gathered using slightly modified instruments in the commercial fleet. A white paper by Boeing has suggested such a study and the group believed a study of this nature should be encouraged.

One comment that was made repeatedly was that the present database, from satellite, aircraft campaigns, and ground-based measurements, is underutilized by the modeling community in testing and improving their models. The use of such data should be encouraged by NASA.

The major part of the discussion centered around measurements of chemical species that could serve as tracers of atmospheric dynamics. These tracers should have fairly simple chemistry with well-understood sources and sinks for each gas. The group also expressed a preference for a tracer that had its source in a well-defined part of the atmosphere. In addition, tracers are needed that represent stratospheric, land, and, if possible, aircraft sources. Rather than focusing on a particular problem in dynamics, it was felt that a program that regularly sampled broad ranges of latitude and longitude would be best. There were two places of particular interest - one in the north Pacific through the Aleutian anticyclone, and the other in the area both north and south of the Himalayas. It is unlikely that one could get regular scheduling through the latter area and so would have to be satisfied with occasional visits.

After much discussion, the group recommended that four airplanes be used and that they fly routes that usually keep them in the following general locations: north Atlantic, south Atlantic, north Pacific, and south Pacific. The group recommended that the airplanes be extended twin-

engine operations (ETOPS), especially outfitted to fly on long-distance routes over water so that they are more likely to remain on the routes we choose.

It was agreed that most chemical problems, particularly those associated with the radicals, are best handled in a process-study mode and so there was no discussion of those species. The focus of discussion was on climatological measurements of the following parameters and selected precision requirements as indicated:

Parameter	Selected Precision Requirements
Temperature	
Pressure	
Horizontal winds	
Latitude, longitude, and altitude	
CH_4 (methane)	1-2 ppbv
N_2O (nitrous oxide)	1-2 ppbv
CO_2 (carbon dioxide)	0.1-0.2 ppmv
CH_3CCl_3 (methyl chloroform)	1-2 pptv
CFC-11	1-2 ppbv
CFC-12	1-2 ppbv
Radon	
Nonmethane hydrocarbons	
Ozone	2 ppbv
H_2O (water)	~2%
NO_x (nitrogen oxides)	10%
NO_y (reactive nitrogen)	10%
HNO_3 (nitric acid)	
^{210}Pb (radioactive isotope of lead)	
Be (beryllium)	
Soot	

It is especially important that the quantities chosen to be measured are ones that have measurement techniques that require very little maintenance and have simple, reliable calibrations. It is expected that one will be able to service the plane at most once a week, and it would be better if that could be done by airline personnel. That requires that the data be self-validating (i.e., requires no skilled operator to determine if the instrument is working properly).

Aside from the measurements that are already available onboard the aircraft and just need to be recorded (temperature, pressure, time, location, and winds), the group recommend that measurements be made of the following: a long-lived tracer (CH_4, CO_2, or N_2O); a short-lived, continental source, tracer (one or more of CFC-11, CFC-12, CH_3CCl_3); a stratospheric tracer; ozone; and, up to the tropopause, H_2O (a species that is very difficult to model). It is desirable that some of these measurements (perhaps ozone and H_2O) be made every 1 km of the flight track. The others should be measured at least every 100 km of the flight track.

The most important thing is reliable measurements. Therefore, it is important to choose techniques with a history of reliability, no use of cryogens, minimal use of calibration gases, no use of dangerous materials, and operation by a serious, dedicated team.

There are only some very rough suggestions as to the cost of such a venture. An initial estimate is $2-3M per year, although this estimate was criticized by some as too small to allow all of the instruments to be built at once and maybe too large for the continuing operation of the instruments. Certainly, once the species are chosen, one can obtain a better estimate.

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Section 7.4

NOx, NOy Data Archive Project

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The Subsonic Assessment (SASS) nitrogen oxide (NO_x), reactive nitrogen (NO_y) archive project began in mid-March 1994. The first task was to decide what data format would be used in the archive. A search of the literature also was made to compile a list of people from whom to request data. In May 1994, a letter was sent to 60 colleagues requesting that they submit the results of their nitric oxide (NO), nitrogen dioxide (NO_2), and NO_y measurements, as well as data for any other species or meteorological parameters measured simultaneously. A copy of the letter is included at the end of this write-up and the investigators contacted are listed in Table 7.4-1. In particular, we requested *in situ* measurements made at non-urban ground sites or by aircraft in the boundary layer, free troposphere, or lower stratosphere. To avoid proprietary questions, we concentrated on data that had already been published and, to avoid duplication, data that had not been archived already (e.g., from the Global Tropospheric Experiment (GTE) and Airborne Arctic Stratospheric Experiment (AASE) campaigns). Table 7.4-1 also indicates whether each researcher contacted had any appropriate data and if the data have been received and incorporated in the archive.

The data format being used is that developed by R. S. Hipskind and S. E. Gaines of NASA Ames Research Center for NASA's stratospheric aircraft campaigns. This format prescribes several ASCII-file formats suited for various types of measurements. Each file format includes a header that contains information about the format of the data portion of the file, as well as particulars about the data itself. The first line of each file gives the number of lines of header in the file and an index identifying the file format. The simplest of these formats is appropriate for most of the data in the archive, and an example is attached at the end of this write-up. Lines 2 through 5 of the file list the investigators' name(s) and institution, a short description of the measurement, and the name of the campaign. The next two lines give an index for the file volume and the total number of volumes (for files larger than a floppy disk, for example) and the dates (year, month, day) of the measurement and analysis. Line 8 gives the time interval between reported measurements, with zero indicating variable intervals, and line 9 is a description of the independent variable (the first column of the data), which is generally the fractional day of the year. The next line gives the number of dependent variables listed in the data, followed by the scale factors and missing data flags for each variable. Scale factors are generally chosen so that data can be listed as integers, representing the significant figures. Missing data values are always larger than any valid data, usually all nines for the number of significant figures given. Each variable name is then given on a separate line with the dimensions of the variable. Below these is space for both special comments, which apply only to the given file, and for normal comments which apply to more than one file (e.g., files for different days of the same measurement during a campaign). Each set of comments is preceded by a line giving the number of lines of comments. We requested that details such as measurement and calibration methods, detection limit and uncertainties, and published references for the data be included in these comments.

It is likely that the final archive will reside at the NASA Langley Research Center Distributed Active Archive Center (DAAC), alongside the GTE archive presently being constructed there. Some reformatting may be necessary to comply with the DAAC's specifications and their software. Table 7.4-2 shows the present contents of the archive, listing the name of the site or campaign, the dates of measurements and the species measured. There are several other datasets that would be a valuable and appropriate addition to this archive, but which were unfortunately not submitted. These are listed in Table 7.4-3.

A policy for users of the archived data was compiled and will be incorporated into the archive so that all users will be aware of it. The policy states:

> Since this is a public archive, freely available to the community, there are no restrictions as to who can gain access to these data. However, there are a few guidelines we urge users of the data to follow, which are based roughly on the NASA Upper Atmosphere Research Program (UARP) and GTE data protocols.
>
> First, it is recommended that the Principal Investigator (PI) for the measurement be contacted to verify proper interpretation of the data for your intended use. Accuracies, uncertainties, detection limits, etc., as well as other special comments or caveats, should be in the headers of the data files, but users are urged to consult the data PIs on the specifics of their use of the data.
>
> Secondly, all users are expected to invite the PI(s) to be co-author on any papers written using his/her/their data, and at least allow them the opportunity to review the use of the data and conclusions drawn from it.

Climatologies of NO_x and NO_y have been developed from these newly archived datasets, along with data from the GTE and AASE campaigns. The data have been grouped by season and altitude (boundary layer and 3-km ranges in the free troposphere). Maps showing median values of midday NO, NO_x, and NO_y have been produced for each season for the boundary layer and 3 km ranges of the free troposphere. The statistics of the data (median, mean and standard deviation, central 67% and 90%) have been determined for each ground site and for small geographical regions of the airborne campaigns. Similar analyses have been done for any ozone and CO data that is available in these datasets, though measurements of these species were not made at all locations.

An announcement of the availability of the archive was published in *Eos* 30 January 1996 ['Access NO_x and NO_y Measurements On-Line,' Volume 77, No. 5, p. 34]. In addition to describing the contents of the archive and how to access it, a figure showing the climatology for midday NO from the boundary layer to 12 km is shown. A draft of the article is attached.

As part of this project, we are preparing a manuscript for publication in the AERONOX special issue in *Atmospheric Environment* presenting climatologies of NO, NO_x, and NO_y. Comparisons with results from five global chemical-transport models are also made. We also have calculated the ratio of NO_x/NO_y where coincident measurements are available and have performed similar analyses on this ratio, calculating the statistics and constructing maps of the median values. The climatology of NO_x/NO_y can help to characterize the typical photochemical age and transport history of air masses at a given site. Climatologies of ozone and CO are being constructed as well, and will be discussed separately.

Continuing studies include examining the climatology of ozone and ozone production. An ozone climatology has been developed with data from the contributed datasets and the GTE archive. The feasibility of determining net ozone production from box model calculations is being tested for sites where limited variables were measured. Tests are being run for datasets where a full

suite of species are available, comparing the model output for runs with more limited inputs. The effect of the large uncertainties in determining photolysis rates must also be assessed before drawing conclusions from the model outputs. The correlations of ozone with NO_x oxidation products (NO_y-NO_x) and ozone with carbon monoxide (CO) also are being examined for trends in the slopes and correlation coefficients to determine if the transport and photochemical history of air masses sampled at the various sites can be characterized.

Table 7.4-1. Researchers contacted. "Data" column indicates whether or not they have appropriate data, and Y under "Received" indicates data has been archived.

Organization and Names	Data	Received
Atmospheric Environment Service, Downsview, Ontario, Canada		
Leonard Barrie		
Stephen Beauchamp	Y	Y
Jan Bottenheim	Y	N
Richard Leaitch	Y	Y
Battelle Columbus Division, Columbus, OH		
Thomas Kelly		
Battelle Pacific Northwest Laboratories, Richland, WA		
Carl Berkowitz	N	
Beijing University, Beijing, China		
Xiao Yang Tang		
Brookhaven National Laboratory, Upton, NY		
Peter Daum		
Larry Kleinman	Y	Y
CEGB Scientific Services, Nottingham, UK		
A. Martin		
Chinese Academy of Meteorological Science, Beijing, China		
Chao Luo	N	
CSIRO Division of Atmospheric Physics, Victoria, Australia		
I. E. Galbally		
DSIR Atmospheric Station, Lauder, New Zealand		
P. V. Johnston		
E. I. DuPont DeNemours & Co., Wilmington, DE		
Mack McFarland	N	
Georgia Institute of Technology, Atlanta, GA	N	
John Bradshaw		
Douglas Davis		
Michael Rodgers		
Scott Sandholm	N	

Table 7.4-1 (continued). Researchers contacted. "Data" column indicates whether or not they have appropriate data, and Y under 'Received' indicates data has been archived.

Organization and Names	Data	Received
Harvard University, Cambridge, MA		
J. William Munger	Y	Y
Steven Wofsy		
Hong Kong Polytechnic, Hung Hum, Kowloon, Hong Kong		
L. Y. Chan	Y	N
Illinois State Water Survey, Champaign, IL		
V. C. Bowersox		
Instituto Nacional de Pesquisas Espaciais, Sao Jose dos Campos, Brazil		
Volker M. Kirchhoff	N	
Institute for Atmospheric Physics, Budapest, Hungary		
E. Meszaros		
KFA Forschungszentrum, Julich, Germany		
Dieter Ehhalt	Y	N
Dieter Kley	Y	N
Andreas Volz-Thomas	Y	N
Daniel McKenna	N	
KFA Karlsruhe, Germany		
H. Fischer		
London Scientific Services, London, UK		
Duncan Laxen	N	
LPCE CNRS, Orleans, France		
Jean Pierre Naudet		
Marine & Atmospheric Sciences Directorate, Swindon, UK		
R. A. Cox		
Max Planck Institut fur Chemie, Mainz, Germany		
Gunter Helas		
Michigan Technological University, Houghton, MI		
Richard Honrath	Y	Y
Nagoya University, Toyokawa Aichi, Japan		
Yutaka Kondo	Y	Y
NASA Ames Research Center, Moffett Field, CA		
Hanwant Singh		
NASA Wallops Flight Facility, Wallops Island, VA		
Arnold Torres	N	
National Park Service, Air Quality Division, Denver, CO		
John D. Ray		

Table 7.4-1 (continued). Researchers contacted. "Data" column indicates whether or not they have appropriate data, and Y under 'Received' indicates data has been archived.

Organization and Names	Data	Received
National Taiwan University, Taipei, Taiwan		
George Chen		
NCAR, Boulder, CO		
Athony Delany		
Brian Ridley	Y	Y
NOAA/Aeronomy Lab, Boulder, CO		
Martin Buhr	Y	N
David Fahey	N	
Gerhard Hübler	Y	N
David Parrish	Y	N
James Roberts	Y	N
Eric Williams	Y	N
NOAA/Air Resources Lab, Silver Spring, MD		
Winston Luke	Y	N
NOAA/AOML/OCD, Miami, FL		
Thomas Carsey	Y	N
NOAA/CMDL, Boulder, CO		
Peter Bakwin	N	
Pennsylvania State University, University Park, PA		
J. P. Shimshock	N	
SUNY Albany, Wilmington, NY		
Kenneth Demerjian	Y	N
Swedish Environmental Research Institute (IVL), Goteborg, Sweden		
Peringe Grennfelt		
Tennessee Valley Authority, Muscle Shoals, AL		
Kenneth Olszyna		
Unisearch, Concord, Ontario, Canada		
John Drummond	Y	N
Harold Schiff	Y	N
Universitat Heidelberg, Heidelberg, Germany		
Uli Platt	N	
University of Alaska, Fairbanks, AK		
Daniel Jaffe	N	
University of Denver, Denver, CO		
Donald Stedman		
University of East Anglia, Norwich, UK		
Stuart Penkett		

Table 7.4-1 (continued). Researchers contacted. "Data" column indicates whether or not they have appropriate data, and Y under 'Received' indicates data has been archived.

Organization and Names	Data	Received
University of Lancaster, Lancaster, UK		
Roy Harrison		
University of Maryland, College Park, MD		
Russell Dickerson	Y	Y
Bruce Doddridge	Y	Y
University of Wisconsin, Milwaukee, WI		
J. D. Kahl		
York University, North York, Ontario, Canada		
Geoff Harriss		
Donald Hastie		

Table 7.4-2. Archived data sets.

Campaign	Type	Date	Species	Location
MLOPEX-1	gnd	May 1-June 4, 1988	all data	Mauna Loa, HI
MLOPEX-2	gnd	Sep 15-Oct 23, 1991 Jan 15-Feb 15, 1992 Apr 15-May 15, 1992 Jul 15-Aug 15, 1992	all data	Mauna Loa, HI
MLOPEX-2	air	Apr 22-May 11, 1992	NO_y, O_3	Hawaii
ELCHEM	air	Aug-Sep, 1991	NO, NO_2, NO_y, O_3	New Mexico
Barrow	gnd	Mar-Nov, 1990	NO, NO_y	Alaska
Shenandoah	gnd	Oct 1988-Oct 1989	NO, NO_y, CO, O_3	Virginia
Harvard Forest	gnd	1990-1993	NO, NO_2, NO_y, O_3, CO	Mass.
SOS/SONIA	gnd	Aug 1991	NO, NO_2, NO_y, O_3, CO	Candor, NC
INSTAC-1	air	March, 1989	NO, O_3	W. Pacific
NARE	air	Aug 9-Sep 7, 1993	NO_y, O_3	Nova Scotia
NAPS	gnd	1980-1992	NO, NO_2, O_3	9 sites BC, Ont
North Bay	air	Jul-Aug, 1988, Mar-Apr, 1990	NO_2, O_3	Ontario

Table 7.4-3. Data sets that have not been submitted.

Campaign/Site	Type	Investigator
Pt Arena, CA	gnd	NOAA/Aeronomy Lab
Niwot Ridge, CO	gnd	NOAA/Aeronomy Lab
Scotia, PA	gnd	NOAA/Aeronomy Lab
Bondville, IL	gnd	NOAA/Aeronomy Lab
Egbert, Ont.	gnd	NOAA/Aeronomy Lab
ROSE	gnd	NOAA/Aeronomy Lab
Whiteface Mt.	gnd	SUNY Albany
TOR/Schauinsland	gnd	KFA Julich
TROPOZ	air	KFA Julich
STRATOZ	air	KFA Julich
PRE-STORM	air	NOAA/Air Resources Lab

16 May 1994

Dear Dr. xxx

Louisa Emmons and I are constructing an archive of NO, NO_2 and NO_y measurements with support from NASA's Subsonic Assessment (SASS) Program. This archive will primarily contain measurements that have not been archived previously and will ultimately be available to the entire community as part of a DAAC housed at Langley. At this point we invite (READ "URGE") you to send us the results of your measurement campaigns, preferably in the format described on the attached pages. We need to obtain *in situ* measurements of NO, NO_2 and NO_y made after 1980, in the troposphere and LOWER stratosphere. We are interested in measurements from primarily non-urban ground-based sites or made in the boundary layer and free troposphere. We will also include any other species or parameters measured simultaneously at the same location. We will be incorporating the DC-8 data from the compiled archives of AAOE, AASE I & II, as well as results from MLOPEX I & II, so there is no need to send us any data that has already been archived by NASA or NCAR.

We have decided to adopt the data file format developed by S. E. Gaines and R. S. Hipskind for the recent NASA airborne campaigns (*e.g.,* AASE). The description of this format, along with some specific comments for this archive, are included as attachments to this letter. While data formatted as per the attached instructions will be greatly appreciated, reformatting your data is not required. To minimize the burden on the community and to reduce the time period in which we receive all data, reformatting of data is a step that can be accomplished here, given the appropriate information regarding the format in which your data is stored. In either case, please be sure to include all of the information that we would like to have in the header of the data files, outlined in Section 3 of the attached document (*i.e.,* measurement technique, detection limit, precision, total uncertainties, and references for where the data has been published).

If you have made any summary analyses, we would like to include those separately. For example, if you have made averages over time, please include the minimum, maximum, mean, median, central 67% and central 90% and altitude of the measurements. We would also appreciate it if you could send us reprints of your published data.

We would prefer to have you FTP your data to us. Please contact Louisa Emmons by e-mail (lemmons@sassarch.sprl.umich.edu) to arrange for the transfer of your data. We would greatly appreciate receiving your data by June 20.

Thank you very much for taking the time to provide your input to this archive. If you know of others who should receive this letter, please pass it on to them, or send us their names. This is a great opportunity for us to get all of the NO_x and NO_y data in one archive! Please help us do just that by sending your data in a timely fashion!

Thank you for your participation.

Sincerely,

Mary Anne Carroll and Louisa K. Emmons

FILE FORMAT EXAMPLE

```
38  1001                                          {No. Header lines, Format index}
Carroll, Mary Anne & D. Dunlap
NOAA Aeronomy Laboratory (present Address:  U.Michigan, AOSS Dept, Ann Arbor MI)
NO+O3 Chemiluminescence Detection
MLOPEX - Mauna Loa Observatory Photochemistry EXperiment, May 1 - June 4, 1988
1  1                                              {Volume index, Total volumes}
1988  05  01  1989  03  10                        {Meas. date, Analysis date}
0                                                 {Data interval, 0=variable}
Julian Day  (fractional, Hawaiian Standard Time)
6                                                 {No. variables}
1.0  1.0  1.0  1.0  0.01  0.01                    {Scale factor for each var}
99  99  99  99  9999  999                         {Value of missing data}
Start time hours (HST)                            {Variable names}
Start time minutes
Start time seconds
Averaging time of measurement  (s)
NO mixing ratio (pptv)
Standard deviation (pptv)
0                                                 {No. lines of special comments}
18                                                {No. lines of normal comments}
   Mauna Loa, Hawaii; Lat 19:32':22.14"  Long 155:34':42.53"  Alt 11134 ft
   Project Scientist- B. A. Ridley, NCAR, Boulder CO 80307; (303)497-1420
   Data compiled By- J. G. Walega, NCAR, Boulder CO  80307; (303)497-1487

This is FREE TROPSPHERE DATA ONLY.  Please see README file in /mlopex1
main directory for description of filtering method used.

PRECISION estimates for 1 minute averages at the 95% confidence limits are:
1.2 pptv at 1 standard deviation
NO zero's were determined by averaging NO from 0000 to 0500 daily.

REFERENCE:  Mary Anne Carroll, Brian A. Ridley, Denise D. Montzka,
Gerhard Hubler, James G. Walega, Richard B. Norton, Barry J. Huebert,
and Frank E. Grahek, Measurements of nitric oxide and nitrogen dioxide
during the Mauna Loa Observatory Photochemistry Experiment,
J. Geophys. Res., 97, 10,361, 1992.
```

Julian Day	Start Time			Duration(s)	NO (pptv*100)	std dev (pptv*100)
122.9167	22	0	2	60	-98	229
122.9174	22	1	2	60	-67	142
.						.
.						.
.						.

Data Archive of NO_x and NO_y Measurements

Louisa K. Emmons and Mary Anne Carroll
Department of Atmospheric, Oceanic and Space Science
University of Michigan
Ann Arbor, MI 48109-2143

An archive has been compiled of previously published, but not publicly archived, *in situ* measurements of NO, NO_2, and NO_y (total reactive nitrogen: NO_x + HNO_3 + PAN + NO_3 + ...). The emphasis has been on obtaining non-urban surface, boundary layer, free tropospheric, and lower stratospheric measurements. Any coincident measurements of other species or parameters (e.g., temperature or winds) also have been included. A summary of the archived data sets is given in Table 7.4-4. The data are presently in a standard ASCII file format and reside on a UNIX workstation. The archive will be accessible eventually from the Langley DAAC and is currently available by anonymous ftp from the University of Michigan. To access the archive, ftp to sassarch.sprl.umich.edu; the archive is in the directory /pub/ARCHIVE}. Please retrieve the text files in this directory for protocol and file format information. Additional information may be obtained by contacting Louisa Emmons (Internet address: lkemmons@umich.edu).

The data protocol is similar to those of other archives. The data in this archive is not considered "proprietary" since it has been published in some form, however all users of the data are encouraged to contact the PI(s) for the data prior to use to verify suitability for the intended work. It is recommended that users, at a minimum, extend the option of co-authorship to the PI on any publications or presentations using their data.

From the newly archived data, along with data from some of the GTE campaigns (Arctic Boundary Layer Expedition (ABLE-3A, -3B); Chemical Instrumentation Test and Evaluation (CITE-2, -3); Pacific Exploratory Mission (PEM-West-A); Transport and Atmospheric Chemistry near the Equator - Atlantic (TRACE-A)) and the AASE I and II campaigns, climatologies of NO, NO_x, and NO_y have been constructed. The data have been sorted by season and 3-km altitude regions, and the statistics (median, mean, central 67%, and central 90%) for these subsets of each campaign have been found. Figure 7.4-1 shows the median values of midday NO for the boundary layer to 3 km, 3 to 6 km, 6 to 9 km, and 9 to 12 km. The stars indicate measurements from ground sites and the shading shows the location of airborne measurements. The stars on Hawaii in the 3- to 6-km map represent measurements at Mauna Loa Observatory (elevation 3.4 km) during "downslope" flow, when free tropospheric air was sampled. The 9- to 12-km data represent tropospheric data, having been filtered using coincident ozone and nitrous oxide (N_2O) or water (H_2O) data.

Information on how to access the GTE archive at NASA Langley is available from James Hoell (gte+archive@larc.nasa.gov) or the Langley DAAC worldwide web page (http://eosdis.larc.nasa.gov/).

Mary Anne Carroll and Louisa Emmons, Department of Atmospheric, Oceanic and Space Science, University of Michigan, Ann Arbor, MI 48109-2143.

Table 7.4-4. Archived data sets, with the location, type (airborne or ground-based), and dates of measurements, along with the species sampled. Explanation of acronyms are given in the notes, with the name and institution of the Principal Investigator(s).

Campaign	Type	Date	Species	Location
MLOPEX-1	gnd	May 1-June 4, 1988	all data	Mauna Loa, HI
MLOPEX-2	gnd	Sep 15-Oct 23, 1991 Jan 15-Feb 15, 1992 Apr 15-May 15, 1992 Jul 15-Aug 15, 1992	all data	Mauna Loa, HI
MLOPEX-2	air	Apr 22-May 11, 1992	NO_y, O_3	Hawaii
ELCHEM	air	Jul 27-Aug 22, 1989	NO, NO_2, NO_y, O_3	New Mexico
Barrow	gnd	Mar-Nov, 1990	NO, NO_y	Alaska
Shenandoah	gnd	Oct 1988-Oct 1989	NO, NO_y, O_3, CO	Virginia
Harvard Forest	gnd	1990-1993	NO, NO_2, NO_y, O_3, CO	Mass.
SOS/SONIA	gnd	Aug 7-17, 1991	NO, NO_2, NO_y, O_3, CO	Candor, NC
INSTAC-1	air	March 5-10, 1989	NO, O_3	w. Pacific
NARE	air	Aug 9-Sep 7, 1993	NO_y, O_3	Nova Scotia
NAPS	gnd	1980-1992	NO, NO_2, O_3	9 sites BC, Ont
North Bay	air	Jul-Aug, 1988, Mar-Apr, 1990	NO_2, O_3	Ontario

1. Mauna Loa Observatory Photochemistry Experiment, Project Scientists: B. A. Ridley, E. L. Atlas, National Center for Atmospheric Research.

2. B. A. Ridley, J. E. Dye, National Center for Atmospheric Research.

3. R. Honrath, D. Jaffe, University of Alaska.

4. B. Doddridge, R. Dickerson, University of Maryland.

5. J. W. Munger, Harvard University.

6. Southern Oxidants Study, SONIA site: Candor, North Carolina, B. Doddridge, R. Dickerson, University of Maryland.

7. International Stratospheric Air Chemistry campaign, Y. Kondo, Nagoya University.

8. North Atlantic Regional Experiment, L. Kleinman, Brookhaven National Lab.

9. National Air Pollution Surveillance, J. Shelton, Environment Canada.

10. R. Leaitch, Atmospheric Environment Service.
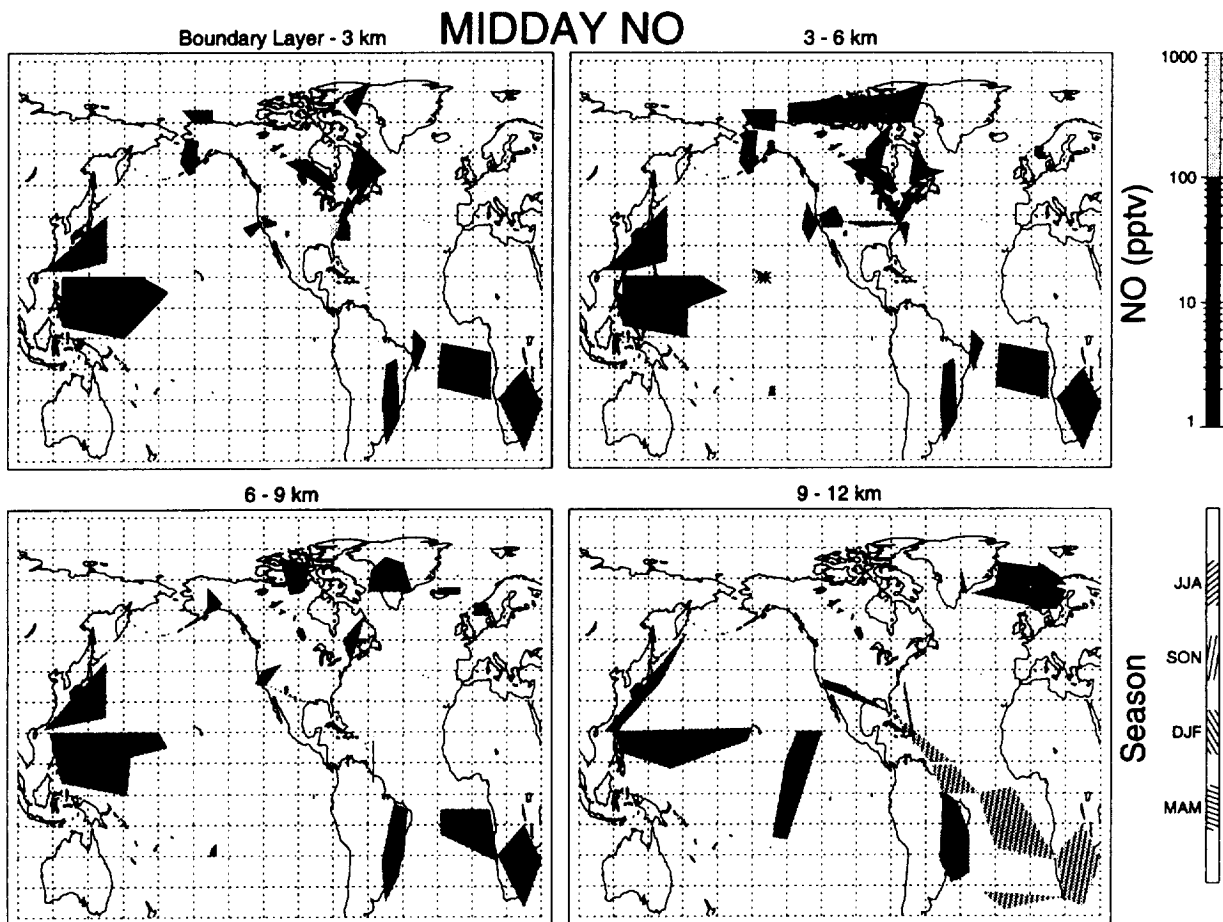
Figure 7.4-1. Median values of midday NO mixing ratios in 3-km altitude ranges. The upper left map includes surface measurements in the boundary layer (indicated by asterisks) as well as airborne measurements between 0.5 and 3 km (shading). For clarity, surface measurements are shown for summer only. Angle of shading indicates the three-month period during which the measurements were made.

Appendix A

SASS Funded Principal Investigators

Table A-1a. Fast-SASS Principal Investigators

Atmospheric Observations

Thomas P. Ackerman	Pennsylvania State University
Elliot L. Atlas	National Center for Atmospheric Research
Alan R. Bandy	Drexel University
John D. Bradshaw	Georgia Institute of Technology
Edward V. Browell	NASA/Langley Research Center
William H. Brune	Pennsylvania State University
Mary Anne Carroll	University of Michigan
David R. Crosley	SRI International
Michael R. Gunson	Jet Propulsion Laboratory
William S. Heaps	NASA/Goddard Space Flight Center
R. Stephen Hipskind	NASA/Ames Research Center
James M. Hoell	NASA/Langley Research Center
Shaw C. Liu	NOAA/Aeronomy Laboratory
Max Loewenstein	NASA/Ames Research Center
Leonhard Pfister	NASA/Ames Research Center
Michael H. Proffitt	NOAA/Aeronomy Laboratory/University of Colorado/CIRES
James C. Ross	NASA/Ames Research Center
Glen W. Sachse	NASA/Langley Research Center
Kenneth Sassen	University of Utah
James D. Spinhirne	NASA/Goddard Space Flight Center
David Starr	NASA/Goddard Space Flight Center
Christopher R. Webster	Jet Propulsion Laboratory
James C. Wilson	University of Denver

Laboratory Studies

Linda R. Brown	Jet Propulsion Laboratory
William B. DeMore	Jet Propulsion Laboratory
Randy D. May	Jet Propulsion Laboratory
Roger E. Miller	University of North Carolina, Chapel Hill
Mario J. Molina	Massachusetts Institute of Technology
Stanley P. Sander	Jet Propulsion Laboratory

Modeling

Guy P. Brasseur	National Center for Atmospheric Research
Charles H. Jackman	NASA/Goddard Space Flight Center
Daniel J. Jacob	Harvard University
Sasha Madronich	National Center for Atmospheric Research
R. Alan Plumb	Massachusetts Institute of Technology
Lamont R. Poole	NASA/Langley Research Center
David H. Rind	NASA/Goddard Institute for Space Studies
Jose M. Rodriguez	Atmospheric and Environmental Research, Inc.
Richard B. Rood	NASA/Goddard Space Flight Center
Ross J. Salawitch	Jet Propulsion Laboratory
Donald J. Wuebbles	University of Illinois

Near-Field Interactions

Lamont R. Poole	NASA/Langley Research Center

Table A-1b. SASS NRA Principal Investigators

Atmospheric Observations

Bruce E. Anderson	NASA/Langley Research Center
Christopher H. Becker	SRI International
David F. Blake	NASA/Ames Research Center
John D. Bradshaw	Georgia Institute of Technology
William H. Brune	Pennsylvania State University
Karen L. Carleton	Physical Sciences Inc.
K. Roland Chan	NASA/Ames Research Center
William A. Cooper	National Center for Atmospheric Research
James W. Elkins	NOAA/Climate Monitoring and Diagnostics Laboratory
Bruce L. Gary	Jet Propulsion Laboratory
Hermann E. Gerber	Gerber Scientific, Inc.
John Hallett	Desert Research Institute
Sonia M. Kreidenweis	Colorado State University
Paul Lawson	Spec, Inc.
Daniel M. Murphy	NOAA/Aeronomy Laboratory
Kevin J. Noone	University of Rhode Island
James R. Podolske	NASA/Ames Research Center
Rudolf F. Pueschel	NASA/Ames Research Center
Kenneth Sassen	University of Utah
Patrick J. Sheridan	NOAA/Environmental Research Laboratories
Robert A. Stachnik	Jet Propulsion Laboratory
Cynthia Twohy Ragni	National Center for Atmospheric Research
Edward E. Uthe	SRI International
Steven C. Wofsy	Harvard University

Exhaust Characterization

Robert P. Howard	Arnold Air Force Base (AEDC)
Ian A. Waitz	Massachusetts Institute of Technology

Laboratory Studies

Jonathan P. D. Abbatt	University of Chicago
John R. Barker	University of Michigan
David R. Crosley	SRI International
Randall R. Friedl	Jet Propulsion Laboratory/NASA Headquarters
Dennis Lamb	Pennsylvania State University
David J. Nesbitt	National Institute for Standards and Technology
Terry W. Rawlins	Physical Sciences Inc.
Margaret A. Tolbert	University of Colorado, Boulder
Leah R. Williams	SRI International

Near-Field Interactions

Bruce E. Anderson	NASA/Langley Research Center
Alan J. Bilanin	Continuum Dynamics, Inc.
Donald E. Hagen	University of Missouri, Rolla
Igor Karol	A. I. Voeikov Main Geophysical Observatory
William S. Lewellen	West Virginia University
Suresh Menon	Georgia Institute of Technology
Richard C. Miake-Lye	Aerodyne Research, Inc.
Andrew A. Sorokin	Scientific and Research Center "ECOLEN"

Global Modeling

Thomas P. Ackerman	Pennsylvania State University
Andrew G. Detwiler	South Dakota School of Mines and Technology
Marvin A. Geller	State University of New York, Stony Brook
Gerald L. Gregory	NASA/Langley Research Center
Matthew H. Hitchman	University of Wisconsin, Madison
David J. Hofmann	NOAA/Climate Monitoring and Diagnostics Laboratory
Ivar S. A. Isaksen	University of Oslo
Daniel J. Jacob	Harvard University
Eric J. Jensen	NASA/Ames Research Center
Douglas E. Kinnison	Lawrence Livermore National Laboratory
Kuo-Nan Liou	University of Utah
Shaw C. Liu	NOAA/Aeronomy Laboratory
Sasha Madronich	National Center for Atmospheric Research
John C. McConnell	York University
Patrick Minnis	NASA/Langley Research Center
Joyce E. Penner	Lawrence Livermore National Laboratory
Kenneth E. Pickering	JCESS, University of Maryland
Michael Poellot	University of North Dakota
Michael J. Prather	University of California, Irvine
Richard Ramaroson	Office National d'Etudes et Recherches Aerospatiales
Philip J. Rasch	National Center for Atmospheric Research
David H. Rind	NASA/Goddard Institute for Space Studies
Jose M. Rodriguez	Atmospheric and Environmental Research, Inc.
Henry B. Selkirk	NASA/Ames Research Center
Hanwant B. Singh	NASA/Ames Research Center
Joel Tenenbaum	State University of New York, Purchase
Richard P. Turco	University of California, Los Angeles
Guido Visconti	Universita' degli Studi L'Aquila
Chris J. Walcek	State University of New York, Albany
Ronald M. Welch	South Dakota School of Mines and Technology

Appendix B

SASS Research Summaries

Note: Summaries are grouped alphabetically by Principal Investigator according to SASS subelements. Where more than one investigator is listed, * denotes Principal Investigator

Development of a Fast-Response, High-Precision, Airborne CO_2 Measurement System for Use in Aircraft Emission Characterization Studies

Investigators

*Bruce E. Anderson
Mail Stop 483
Atmospheric Studies Branch
Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23681-0001

Glen W. Sachse
James E. Collins, Jr.
Mail Stop 472
Sensor Systems Branch
Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23681-0001

Research Objectives

We proposed to add high-precision CO_2 measurement capability to the SASS-funded airborne tunable diode laser (TDL) CO and CH_4 detection system presently under construction at NASA Langley Research Center (LaRC). This capability would be provided by a modified commercial non-dispersive infrared (NDIR) CO_2 monitor similar to the one adapted by the investigators and used successfully aboard the NASA Ames DC-8 during the NASA Global Tropospheric Experiment Pacific Exploratory West (PEM-West A) and Transport and Atmospheric Chemistry near the Equator - Atlantic (TRACE-A) missions and the Second Airborne Arctic Stratospheric Expedition (AASE-II). The CO_2 instrument used in those programs provides a precision of +.05 ppmv (+1σ) at a response rate of 1 Hz. The new CO_2 instrument, which will share rack space and flow/data system components with the new SASS-TDL system, will incorporate additional thermal controls and electronic features to improve its precision at high sampling frequencies with the ultimate goal of achieving +0.05 ppmv precision at a response rate of 10 Hz.

Summary of Progress and Results

An NDIR CO_2 instrument was purchased from LiCor during summer 1994 and modified as follows:

- The standard flow system fittings were replaced with stainless steel compression fittings to facilitate operation of the unit at sub-ambient pressure.

- The output wires were replaced with coaxial cable to provide better shielding against noise.

- The output signal amplifier was modified to provide 100 Hz low-pass filtering and an additional factor of 3 gain.

- A 10-Hz, 8-pole, Bessel-type filter was added to the signal output section to reduce noise from the on-board switching power supply.

- The unit was wrapped in thermal insulation and thermostated heaters were installed on its base and the air intake duct to provide thermal control to within ±0.5°C.

The modified instrument was set up with a pressure and flow controlled flow system and tested for precision, noise, and response time. The peak-to-peak noise level of the system when sampling gas of a constant CO_2 concentration was < 0.1 ppmv for an electronic response time of 10 Hz. Precision was calculated as the standard deviation of 200 data points collected over a 1 second period when sampling

gas of a constant concentration. Typical values fell in the range of 0.03 to 0.05 ppmv which meet or exceed our original design goal. The long term precision, calculated as the standard deviation of 100, 1-second averages was also < 0.05 ppmv. The system will be further evaluated during field tests onboard the NASA Wallops Sabreliner aircraft in spring 1995 and upon a flux tower in summer 1995. The finalized unit will be installed within the LaRC TDL system and deployed aboard the NASA DC-8 during the spring 1996 SASS-sponsored SUCCESS mission over Oklahoma.

Publications

None

Trace Gas Measurements for Whole-Air Sampling

Investigator

Elliot L. Atlas
National Center for Atmospheric Research
P. O. Box 3000
Boulder, CO 80307-3000

Research Objectives

Our primary research objectives for 1994 were to refine our calibrations of various organic halogens and to continue data analysis.

Summary of Progress and Results

Our laboratory work involved assessments and refinements of our calibrations for CH_3Br, CFC 115, Halon-1301, and HCFC-141b. We also participated in successful intercalibrations for HCFC-141b and CH_3Br with the NOAA Climate Monitoring and Diagnostics Laboratory. Additional laboratory work involved the design and construction of automated inlet systems for some of our analytical instruments and modifications to the GC/MSD to improve our precision for CFC-115 and Halon-1301.

Our data analysis involved both tropospheric and stratospheric datasets. We reported a strong latitudinal gradient of HCFC-141b mixing ratios in the marine boundary layer from samples collected during a cruise in the Pacific. Average HCFC-141b mixing ratios in April 1993 in the northern and southern hemispheres were 0.83 ± 0.23 pptv and 0.28 ± 0.07 pptv, respectively. The data from the cruise, together with data collected during AASE II, allowed us to calculate global emissions of HCFC-141b for 1990-1993 using a two box model. We also found a north/south latitudinal gradient of 1.3 in CH_3Br mixing ratios from a composite of cruise data. We are continuing our analysis of the distribution of CH_3Br in the upper troposphere and lower stratosphere.

We evaluated the age of stratospheric air, relative to the time of entry from the troposphere, using CFC-115 and CO_2 mixing ratios from AASE II. Calculations using both species gave similar results. Between 325 K and 500 K air outside the polar vortex was between 1 and 4 years old while air inside the vortex was between 4 and 6 years old. The deduced ages were used with concurrent measurements of organic chlorine and bromine containing halocarbons to determine inorganic chlorine and bromine as a function of latitude and altitude. We are in the process of comparing these calculations with those of a 2-D interactive dynamical/radiative/chemical model. We are also continuing our analysis of the distribution of halocarbons in the lower stratosphere.

In addition to our data analysis and lab work, we have suggested a physical mechanism that may influence the trends of trace gases. Specifically, we show that if heating from volcanic aerosols were of sufficient magnitude to significantly increase stratospheric circulation, the response in the troposphere would be a decline in the increasing trends of N_2O and CH_4. The decline results from a higher degree of exchange between the stratosphere, which contains lower mixing ratios of both gases, and the troposphere.

Publications

Avallone, L. M., D. W. Toohey, S. M. Schauffler, W. H. Pollock, L. E. Heidt, E. L. Atlas, and K. R. Chan, *In situ* measurements of BrO during AASE II, *Geophys. Res. Lett., 22,* 831-834, 1995.

Schauffler, S. M., and J. S. Daniel, On the effects of stratospheric circulation changes on trace gas trends, *J. Geophys. Res., 99,* 25747-25754, 1994.

Schauffler, S. M., W. H. Pollock, E. L. Atlas, and L. E. Heidt, Atmospheric distributions of HCFC 141b, *Geophys. Res. Lett., 22,* 819-822, 1995.

Woodbridge, E. L., J. W. Elkins, D. W. Fahey, L. E. Heidt, S. Solomon, T. J. Baring, T. M. Gilpin, W. H. Pollock, S. M. Schauffler, E. L. Atlas, M. Loewenstein, J. R. Podolske, C. R. Webster, R. D. May, J. M. Gilligan, S. A. Montzka, K. A. Boering, and R. J. Salawitch, Estimates of total organic and inorganic chlorine in the lower stratosphere from *in situ* and flask measurements, *J. Geophys. Res.*, *100*, 3057-3064, 1995.

Development of High Speed/High Sensitivity Laser-Induced Fluorescence Measurement Capabilities for Reactive Nitrogen Compounds

Investigators

*John D. Bradshaw
Scott T. Sandholm
School of Earth and Atmospheric Sciences
Georgia Institute of Technology
925 Dalney Street
Atlanta, GA 30332-0340

Research Objectives

The primary objective of this research is the development and testing of an ultra sensitive, fast temporal response sensor for measuring oxides of nitrogen in the upper troposphere/lower stratosphere. This sensor capability will enable exploitation of the information contained in the chemical fine structure of the atmosphere. The sensor design is targeted for providing high precision ($< \pm 5\%$), high speed (≥ 10 Hz) measurements at levels as low as 10 pptv. This level of performance will enable high speed cross-correlation techniques (e.g., dO_3/dt and dCO/dt versus dNO/dt) to be applied to the interpretation of NO source signature characterizations, even well downwind of air traffic corridors or convective cloud outflows. In addition, this sensor's sensitivity will enable relatively small quantities of ^{15}NO to be used as a sensitive real-time tracer in a number of atmospheric and aircraft effects process studies.

Summary of Progress and Results

Since this project's beginning in December 1994, we have focused our efforts on characterizing a first generation sensor's response at low levels of NO and on characterizing, under a variety of conditions and using a number of surrogate NO_y compounds, the performance of various NO_y converters that might be compatible with the new sensor design. This effort has resulted in demonstrating a quantitative and linear NO instrument response from >10 ppbv down to the levels of 1 pptv. Quantitative sub-pptv studies are also planned, along with further sensitivity improvements in order to test the sensor's behavior for low level ^{15}NO tracer studies. We have also initiated an extensive series of studies aimed at characterizing an NO_y converter that will be compatible with the final sensor, and one that will have a rapid response time. These studies include characterizing, under a variety of atmospheric sampling conditions, the conversion efficiency of a number of surrogate NO_y compounds and potential interferences, using both Au and MoO converters. In addition, design work has been initiated for reducing the LIF sensor's size by approximately a factor of two.

Publications

None

Airborne DIAL Renovation and Upgrade

Investigator

Edward V. Browell
Mail Stop 401A
Chemistry and Dynamics Branch
Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23681-0001

Research Objectives

To renovate and upgrade the NASA Langley Research Center (LaRC) airborne differential absorption lidar (DIAL) system and complete a second airborne DIAL system for future Subsonic Assessment (SASS) field experiments. Changes to the airborne DIAL system will substantially increase the capability and reliability of the current system for the simultaneous measurement of ozone and aerosol distributions from the surface to above the tropopause.

Summary of Progress and Results

New lasers were purchased and installed in the airborne DIAL system. These Continuum Nd:YAG-pumped dye lasers are capable of 30 Hz operation at 85 mJ per pulse in the UV. This is a six-fold increase over the average power of our old lasers. This change will improve our ozone measurement accuracy and increase the range of our measurements by more than a factor of two. There is also a significant increase in the laser energy at the visible and infrared wavelengths for the aerosol measurements. In addition, the new lasers have fewer flashlamps and easier maintenance features, along with newer optical and mechanical designs. A new laser base structure was designed and built, and the completed laser transmitter system is shorter and lighter than the old one. A new, larger-capacity heat exchanger was purchased for the new lasers. This type of exchanger operates on 400 Hz aircraft power, which is more efficient than the 60 Hz operation of the old heat exchanger. A new energy monitor system and a new computer-controlled beam steering system were designed. The data system was upgraded to be able to calculate, display, and color copy more reduced DIAL data in real time and electronically distribute it to other CRT's around the aircraft. Changes are being made to the old DIAL system to improve its temperature stability and optical damage susceptibility. All the necessary components for a second identical data system are in hand.

In the next six months, the new laser transmitter system will be test flown on the Wallops P-3 aircraft, the renovations and upgrades to the old DIAL system will be completed, the second dual-telescope receiver system will be completed, and the second DIAL system will be prepared for flight tests in early 1996. Both DIAL systems will be available for simultaneous use on different aircraft for the joint SASS-GTE PEM West-Tropics field experiment in the summer of 1996.

Publications

None

Airborne DIAL Data Analysis

Investigators

*Edward V. Browell
William B. Grant
Mail Stop 401A
Chemistry and Dynamics Branch
Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23681-0001

Research Objectives

To analyze airborne differential absorption lidar (DIAL) data from the PEM-West-A, AASE-II, and TRACE-A field experiments for information on lower stratospheric dynamics and stratosphere-troposphere exchange (STE) processes. The presence of enhanced aerosols in the lower stratosphere due to the eruption of Mount Pinatubo in June 1991 provided a tracer for the transport and decay of aerosols in the lower stratosphere and in STE processes. This task will also investigate the correlation between ozone and potential vorticity distributions in the troposphere resulting from STE processes.

Summary of Progress and Results

Airborne DIAL ozone and aerosol data from the AASE-II, PEM-West A, and TRACE-A field experiments were analyzed for information related to dynamics in the lower stratosphere and STE processes. The results of these investigations were presented at the 1995 AEAP Conference held in Virginia Beach on 24-28 April 1995. The observation and interpretation of transport of aerosols in the tropics using the airborne DIAL aerosol data are discussed in the publication cited below. The STE analysis is nearing completion, and the following paragraph summarizes the results to date.

Evidence of STE was observed in the DIAL data on several flights in each field campaign. Strong stratospheric intrusions could be identified by the enhanced aerosol backscattering in the stratospheric air as well as from the elevated O_3 levels. On 60 percent of the PEM-West A flights, O_3 was observed to exceed the background O_3 levels in regions that were determined to be associated with STE. PEM-West A provided the first opportunity for a detailed characterization of the stratospheric air that was being transported into the troposphere at mid and low latitudes over the Pacific. Fewer cases of STE were observed over the tropical southern Atlantic during TRACE-A; however, on one occasion the DC-8 passed through a strong intrusion for a comprehensive chemical characterization of the event. The airborne lidar measurements of O_3 and aerosol distributions showed the vertical distribution of the STE events observed during these field experiments, and this was compared to the meteorological analysis of potential vorticity (PV) fields along the flight tracks. The ratio of PV to ozone in the troposphere was found to be nearly the same as found in the lower stratosphere (~5). A paper on these results is in preparation.

Publications

Grant, W. B., E. V. Browell, C. S. Long, L. L. Stowe, R. G. Grainger, and A. Lambert, Use of aerosols resulting from volcanic eruptions to study the tropical stratospheric reservoir, its boundary, and transport to northern latitudes, submitted to *J. Geophys. Res.*, 1995.

Augmentation to Participation as the Mission Scientist for MAESA

Investigator

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Research Objectives

In situ observations of chemical species from the high-altitude NASA ER-2 aircraft have proved to be essential for understanding stratospheric processes, both the photochemistry and the dynamics. This aircraft and the instrumentation that it carries can provide valuable information about the processes occurring around the tropopause as well, a region of intense interest for the assessment of the effects of the current subsonic fleet. Processes of greatest interest include stratosphere - troposphere exchange, tropical - middle latitude exchange, and changes across the tropopause in the photochemistry that affects ozone. Such observations were scheduled as part of the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) mission that occurred throughout 1994.

Equally important is the use of these results to improve the photochemistry and dynamics in current models. These results can be used two ways. First is direct comparison of local observations with the large-scale model results. Second is applying the insights into atmospheric processes gained by the observations to improve the photochemistry and dynamics of the models. Thus, flights plans were devised to optimize the use of the observations for these models.

Summary of Progress and Results

The ASHOE/MAESA mission concluded successfully in November 1994. The observations from 45 flights span from 60° N to 70° S and include for the first time planned flights deep into the tropics. Vertical profiles that extend into the troposphere were obtained routinely during the tropical flights and at middle latitudes in the Northern and Southern Hemisphere. Both reactive gases and long-lived tracers were measured across the tropopause. These observations are now being analyzed to learn about the photochemistry and dynamics of the tropopause region. The preliminary results have been discussed in the ASHOE/MAESA End-of-Mission Summary.

Efforts to incorporate this information into large-scale models is just beginning. The first results of applying these observations to the models can be expected by the end of 1995.

Publications

None

Adaptation of an *In Situ* Ground-Based Tropospheric OH/HO$_2$ Instrument for Aircraft Use

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Research Objectives

The research objective is to build and test an instrument to measure OH and HO$_2$ from the NASA DC-8 aircraft. This instrument is based on a ground-based design in which OH is detected by laser induced fluorescence in a detection chamber at low pressure. HO$_2$ is detected by chemically conversion with reagent NO followed by LIF detection of the resulting OH. This ground-based design, based on that of Hard and O'Brien, has been shown to be capable of detecting 1.4×10^5 molecules cm^{-3} (S/N = 2) in an integration time of 30 seconds with negligible interferences. The objective is to reconfigure the ground-based system to one compatible with the DC-8 and to couple it to an inlet that slows the air speed from the DC-8 airspeed of 230 m s^{-1} to 20 m s^{-1} for sampling.

Summary of Progress and Results

We have focused on four areas for the modified instrument. First is the development of a laser system that is more compatible with the aircraft environment than that used in the ground-based prototype. Two laser systems, both based on solid-state technology, are being evaluated. Second is the design of a sampling inlet. Computational analysis and wind tunnel testing is being conducted by Kevin James at NASA Ames Research Center. Third is the improvement of computer control and data collection. This system, using components designed by T. Thompson at the NOAA Aeronomy Laboratory, has been modified for our fast, gated detection scheme and is almost complete and tested. Fourth is the modification of the instrument structure for the aircraft. Basic concepts exist for the structure and the location on the aircraft. Final design awaits the selection of the laser system and the completion of the studies on the sampling nacelle design.

We are making progress in all areas and the instrument is on schedule for completion by early 1996.

Publications

None

Single Particle Studies of Heterogeneous Chemistry on Aerosols

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Research Objectives

The engines of high-flying subsonic aircraft emit carbonaceous exhaust aerosols and sulfate aerosol precursors which can alter chemical and radiative balances in the upper troposphere and lower stratosphere. Of particular interest is the formation, growth, and subsequent chemical activity of H_2SO_4 aerosols formed in aircraft engine exhaust plumes. This can be initiated by homogeneous nucleation, or by heterogeneous nucleation on soot particles.

The objective of this project is to perform detailed laboratory investigations of the kinetics of activation, growth, and chemical reactivity of single-particle sulfate and carbonaceous aerosols. Specific chemical behavior to be observed for both carbonaceous and sulfuric acid particles includes hydration, supercooling/freezing, and reactivity toward NO_x/HNO_3. The experiments will employ laboratory-generated H_2SO_4/H_2O particles, "model" carbon particles of well-characterized surface area, and combustion-generated carbon particles. The results of these fundamental laboratory measurements will be directly applicable to the interpretation of field data and to modeling calculations of chemical and radiative impacts.

Summary of Progress and Results

Recent and current work in our laboratory has addressed the freezing behavior of binary H_2SO_4/H_2O aerosols in both stratospheric and tropospheric conditions, and the hydration behavior of carbon and soot particles. In preparation for a measurement series on ternary $HNO_3/H_2SO_4/H_2O$ particles, we have measured the Raman scattering spectra of bulk solutions of H_2SO_4/H_2O, HNO_3/H_2O, and $HNO_3H_2SO_4/H_2O$ as functions of composition and temperature down to ≈ 200 K. These measurements provide new fundamental data on line broadening and spectral distributions for these mixtures at low temperatures. The results will be used to interpret single-particle composition measurements for the binary and ternary mixtures as functions of temperature.

Our previous carbon hydration experiments showed that black carbon particles can be activated towards H_2O uptake by adsorption of H_2SO_4 vapor. We have begun a series of measurements to investigate the dependence of this effect on carbon particle type, dosing conditions, and dosant species such as SO_2, NO_2, and HNO_3. We have developed an approach for interpreting the hydration results in terms of Köhler theory, which relates subsaturation particle hydration kinetics to the critical supersaturation beyond which the particle grows without bound. In this way we will be able to assess the significance of hydrated carbon particles as cloud condensation nuclei (CCN).

Publications

Carleton, K. L., D. M. Sonnenfroh, W. T. Rawlins, B. E. Wyslouzil, and S. Arnold, Chemical and physical properties of sulfuric acid and carbon particles in a quadrupole trap, AAAR Fourth International Aerosol Conference, UCLA, 1994.

Carleton, K. L., D. M. Sonnenfroh, B. E. Wyslouzil, and W. T. Rawlins, Activation of carbon aerosol by deposition of sulfuric acid, 1994 Fall Technical Meeting of the Eastern States Section of The Combustion Institute, Clearwater Beach, FL, 1994.

Carleton, K. L., D. M. Sonnenfroh, W. T. Rawlins, and B. E. Wyslouzil, Activation of carbon aerosol by deposition of sulfuric acid, AGU Chapman Conference on Biomass Burning and Global Change, Williamsburg, VA, 1995.

Compilation of NO_x, NO_y Data Archive

Investigators

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Research Objectives

The objective of this project was to compile an archive of *in situ* measurements of NO, NO_2 and NO_y, made at non-urban ground sites or by aircraft in the boundary layer, free troposphere or lower stratosphere. Climatologies of NO, NO_x, NO_y and ozone have been developed from these newly archived datasets, along with data from GTE and AASE campaigns.

Summary of Progress and Results

Sixty colleagues were contacted, requesting that they send us the results of their measurements of NO, NO_2 and NO_y, as well as data for any other species or meteorological parameters measured simultaneously. To avoid proprietary questions we concentrated on data that had already been published, and to avoid duplication, data that had not been archived already (e.g., from the GTE and AASE campaigns). The header of each data file contains the names and organizations of the investigator, along with descriptions of the variables included in the file. There is also space for as many comments as are needed and the details of the measurement and calibration methods, detection limit and uncertainties, and published references for the data have been given here, along with any additional caveats provided by the investigators.

The archive presently contains year-round measurements from Barrow, AK; Shenandoah National Park, VA; Harvard Forest, MA; and nine rural sites in British Columbia and Ontario (part of the National Air Pollution Surveillance); shorter-term ground measurements from Candor, NC; and airborne measurements in the western Pacific (INSTAC-1); North Atlantic (NARE); and Ontario. The NCAR archives of MLOPEX 1 and 2 have also been incorporated. It is likely that the final archive will reside at the NASA Langley Distributed Active Archive Center (DAAC), alongside the GTE archive presently being constructed there.

Climatologies of NO_x and NO_y have been developed from these newly archived datasets, along with data from the GTE and AASE campaigns. The data have been grouped by season and altitude (boundary layer and 3-km ranges in the free troposphere). Maps showing median values of midday NO, NO_x and NO_y have been produced for each season for the boundary layer and 3-km ranges of the free troposphere. The statistics of the data (median, mean, and standard deviation, central 67% and 90%) have been determined for each ground site and for small geographical regions of the airborne campaigns. Similar analyses have been done for any ozone and CO data that is available in these datasets, though measurements of these species were not made at all locations.

In completion of this project we are preparing a manuscript for publication in *Journal of Geophysical Research* presenting these climatologies of NO, NO_x and NO_y. We have also calculated the ratio NO_x/NO_y where coincident measurements are available and have performed similar analyses on this ratio, calculating the statistics and constructing maps of the median values, and these will also be discussed. The NO_x and NO_y climatologies will be compared with model results from GFDL (H. Levy and P. Kasibhatla) and Lawrence Livermore Laboratory (C. Atherton and S. Sillman).

Publications

Emmons, L., and M. A. Carroll, Data archive of NO_x and NO_y measurements, (An announcement of the availability of the archive, describing the contents of the archive and how to access it), submitted to *Eos*, 1995.

A Meteorological Measurement System (MMS) for the NASA DC-8 Aircraft

Investigators

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Research Objectives

The objective of this task is to develop a Meteorological Measurement System (MMS) on the DC-8 aircraft to provide high-quality, high-resolution meteorological parameters (temperature, pressure, and the three-dimensional wind vector).

Summary of Progress and Results

- The three-year budget of the proposal, entitled "A Meteorological Measurement System for the NASA DC-8 Aircraft", was revised to include only instrument development (design, fabrication, installation, integration, testing, calibration). The cost for the MMS to participate in the SASS field measurement program is not included in the revised budget.

- Airflow angle sensors (Rosemount 858Y units), pressure transducers, temperature probes and backups have been procured. Locations of the Rosemount 858Y probes were determined with the aid of computational fluid dynamics (CFD) modeling. Through negotiation and discussion with DC-8 managers and Serve-Air (DC-8 Contractor) engineers, it is most probable that the a separate plumbing will be installed for the MMS static and dynamic pressure measurements.

- Four antenna and a receiver of the TANS Vector Global Position System (GPS) of Trimble Inc. have been procured; they will be mounted in a diamond configuration on top of the DC-8 fuselage. Measurements from this differential GPS will complement the measurements from the Litton LTN-72RH inertial navigation system (INS). The Litton LTN-72RH INS, as all stable-platform units, has a 84-min Schuler oscillation of 1-2 m s^{-1}.

- Computer boards and electronics for the data system have been ordered. Software for data acquisition and data analysis will be very similar to that of the ER-2 MMS. Locations selected for the data system and the INS have been approved by DC-8 managers and contractors.

- We plan to test fly and calibrate the DC-8 MMS in the first quarter of FY96. We expect that the DC-8 MMS will be ready to participate in the first SASS field measurement campaign, being planned for the second or third quarter of 1996.

Publications

None

NO$_y$ Instrument and Measurement Workshop

Investigator

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Research Objectives

Whether the troposphere forms a net sink or source for ozone is an unanswered question of major importance. On a local scale, the production rate of ozone depends sensitively on the concentration of NO$_x$ present. NO$_x$ is produced by anthropogenic activities, primarily through combustion in the boundary layer over continents; but it can be converted to less reactive compounds (e.g., HNO$_3$ and PAN) and transported large distances, then converted back to NO$_x$ in the remote troposphere. Aircraft exhaust, however, inject NO$_x$ directly into the upper troposphere. This is one of the major environmental effects of subsonic aircraft. An assessment of these effects, in both the unperturbed and perturbed atmosphere, requires accurate measurement of all reactive nitrogen compounds. However, previous missions have revealed problems in the measurement of many of these species, as well as total NO$_y$, at levels found in the remote troposphere. This project convened a workshop, held in December 1993, to identify issues and problems in these measurements.

Summary of Progress and Results

In situ measurements of reactive nitrogen compounds were examined by a panel of forty worldwide experts; the emphasis was on airborne determinations in the free troposphere. It was concluded that there were problems in the measurement of nearly all compounds except NO. Some specific conclusions:

- Total NO$_y$: Detection via NO is not a problem, but there are many concerns about inlet and sampling lines, and the variation of conversion efficiency with ambient conditions. Calibration and zero checks should be improved and performed in-flight. The drafting of a set of guidelines for NO$_y$ instruments was recommended.

- HNO$_3$: There is a wide variety of methods available; measurement precision or limits of detection (10-20 pptv) is not an issue but accuracy is. The major problem is adsorption/desorption on sample and inlet lines, and their variation with ambient conditions. HNO$_3$ can be measured reliable above 1 ppbv but not credibly below 100 pptv. Tunable diode laser detection at low concentrations should be revisited.

- PAN and organic nitrates: Gas chromatographs, used for all PAN measurements is not an issue, but a different approach would be welcome. Care must be taken in calibration. Organic nitrates are present at low concentration and many (perhaps 100) different compounds; differentiation may not be worthwhile for airborne instrumentation.

- Inlets and sampling lines: Tests must be performed for many conditions. Transmission below 100 percent is acceptable if the loss is small and known for all conditions. The sampling port must be in the free stream. Fast, large flows eliminate inlet problems but are difficult to calibrate and zero in-flight.

- Calibration, zeroes, and artifacts: Calibrations and zero checks must be performed under ambient conditions, including humidity. Artifacts so large that their existence and correction may alter scientific conclusions require redesign of the instrument.

Publications

Crosley, D. R., *Issues in the Measurements of Reactive Nitrogen Compounds in the Atmosphere*, SRI International Report MP 94-035, 1994.

Microwave Temperature Profiler Studies in Support of Subsonic Assessments

Investigator

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Research Objectives

This task consists of hardware modifications to reduce the size of an existing DC-8 remote sensing instrument, the Microwave Temperature Profiler for the DC-8 aircraft (MTP/DC-8). The MTP/DC-8 instrument consists of a 50 pound "sensor unit" and approximately 150 pounds of rack-mounted equipment constituting a "data unit." This task will replace the rack-mounted equipment with a compact 13-pound data unit. By mounting the new data unit to the side of a nearby rack, or possibly to the sensor unit, we will "free up" an entire rack for other users. This savings of space is motivated by the pressure of ever greater numbers of experiments that need to be flown aboard the DC-8 in support of subsonic assessment studies.

MTP/DC-8 flight objectives are to measure air temperature versus altitude every 15 seconds. The altitude region for which temperatures exhibit a < 2 K RMS has been shown on previous flights to be 12-km thick, i.e., from 6 to 18 km while flying at 11 km. With this information it is possible to monitor the altitude of the tropopause, identify passage through (or underneath) the subtropical jet, identify tropopause folds, and detect mountain waves.

Summary of Progress and Results

Approximately 60 percent of the hardware modifications have been completed. The goal is to be flight ready before the DC-8s October SASS flights. It is likely that the new MTP/DC-8 will be ready for the May 1995 SASS test flights.

Publications

None

Characterization of Aircraft Produced Soot and Contrails Near the Tropopause

Investigators

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Research Objectives

The purpose of the research is to characterize nuclei from aircraft exhausts in terms of their ability to form cloud droplets and subsequently ice crystals, and also to characterize the ice crystals produced as near growth in the contrail and as far growth as the contrail mixes with its environment. This is accomplished by direct (*in situ*) measurement of condensation nuclei (CN) by a standard TSI instrument (model 3010) by measurement and, of cloud condensation nuclei (CCN) by a specifically designed spectrometer which provides the number of nuclei active at specific supersaturation. Ice crystals are characterized by two instruments. A cloudscope collects crystals (down to a few μm) on a forward facing optical flat. Crystals are viewed from behind and video recorded; they evaporate under stagnation conditions. This instrument gives mass, and, shape and concentration over the range approximately 2 μm to 500 μm. Particle density may also be deduced. The second instrument, a formvar replicator, makes casts of each crystal for subsequent analysis, from which size, shape and concentration can be deduced, and enables high-resolution microscopy and scanning electron microscopy to be carried out. Instrumentation is being readied for field testing and deployment on the DC-8.

Summary of Progress and Results

- Racks have been designed and built according to NASA specification for installation on the NASA DC-8 to hold the CCN spectrometer, the CN counter, its thermal analyzer and calibration electrostatic classifier. These racks also hold the controls and display units for the cloudscope and replicator. These units will be subject to NASA inspection in April 1995.

- The CCN spectrometer has been modified to work at supersaturation beyond 0.8 percent, and down to 2 percent. This enables a more realistic spectrum to be obtained of soot. A few percent of the particles are active at supersaturation of less than 0.8 percent; preliminary results show that there is a rapid rise of activation with supersaturation, to 20 percent active at 2 percent supersaturation.

- Laboratory tests at these higher supersaturations of thermally characterized soot by heating to temperatures up to 600° C will enable characterizing the impurity which gives rise to the effective CCN.

- The cloudscope was flight tested after modifications in the NCAR C-130 in December. As a result of these tests it will be further modified in internal layout for flight testing in the DC-8 in June/July 1995.

- The replicator has undergone modification in formvar supply systems and is ready for flight tests in the DC-8. It was previously flown on the DC-8 in TOGA COARE and modifications were made in view of these results to give a longer running time. Preliminary work is underway on chemical identification of aerosol constituents by spot reactions. This instrument will be mounted and test flown on the DC-8 in June/July 1995.

Publications

Arnott, W. P., Y. Y. Dong, and J. Hallett, Extinction efficiency in the infrared (2-18 μm) of laboratory ice clouds: Observations of scattering minima in the Christiansen bands of ice, *J. Applied Optics, 34*, 541-551, 1995.

Arnott, W. P., Y. Y. Dong, J. Hallett, and M. R. Poellot, Observations and importance of small ice crystals in a cirrus cloud from FIRE II data, *J. Geophys. Res., 99*, 1371-1381, 1994.

Foster, T., W. P. Arnott, J. Hallett, J. G. Hudson, and R. Pueschel, Measurements of ice particles in tropical cirrus anvils: Importance in radiation balance, Conference Cloud Physics, Dallas, TX, AMS Preprints, 1995.

Hallett, J., J. G. Hudson, B. Queen, and E. Teets, Aerosol and cirrus opacity, 33rd Aerospace Sciences Meeting, Reno, NV, AIAA Paper No. 95-0544, 1995.

Hallett, J., B. Queen, E. Teets, and J. Fahey, *Nucleation Growth of Crystals under Cirrus and Polar Stratospheric Cloud Conditions,* Technical Report, 1995.

Airborne Raman Lidar for Measurement of Atmospheric Trace Constituents

Investigators

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Research Objectives

The airborne Raman lidar will make simultaneous measurements at 5 wavelengths scattered by the atmosphere from a single transmitted wavelength. The five wavelengths arise from Rayleigh and Mie scattering which yield information about atmospheric number density and aerosol content plus Raman scattering from nitrogen, oxygen, methane and water vapor. Number densities of methane and water vapor are of intrinsic interest to the AEAP/SASS program. Since these species are major effluents from aircraft engine exhaust and are quite long lived they would be particularly useful for diagnosing corridor effects in aircraft exhaust. Nitrogen and oxygen Raman signals provide a very accurate atmospheric number density measurement that is relatively untainted by aerosol composition of the atmosphere. This number density measurement can be used to infer both temperature and pressure along the lidar ranging direction. In summary, we propose to implement an airborne measurement system with the capability to sample methane and water vapor concentration as well as temperature and pressure over a two dimensional field defined by the upward range of the lidar and the track of the aircraft. These measurements will be applied to searches for corridor effects produced by current commercial aircraft traffic.

Summary of Progress and Results

A series of test flights were conducted with the lidar operating from the C-130 aircraft operated by NASA Wallops Flight Center. These missions demonstrated the ability of the instrument to measure methane, water vapor and temperature under aircraft conditions. The instrument is presently undergoing changes in configuration aimed at improving performance and to permit operation from the DC-8 aircraft which has superior capabilities with regard to measurement missions.

Publications

Heaps, W. S., and J. F. Burris, Airborne Raman Lidar, submitted to *Applied Optics,* 1995.

Transfer of the NASA Global Troposphere Experiment (GTE) Data Archive to the Langley Distributed Active Archive Center (DAAC)

Investigator

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Research Objectives

To reformat and transfer data acquired during GTE field missions to the Langley DAAC.

Summary of Progress and Results

The GTE data archive, which is maintained through the GTE Project Office at the Langley Research Center, currently contains results from the following GTE field missions.

MISSION	LOCATION	DATE
ABLE -1	Tropical Atlantic, Barbados	1984
CITE-1	Eastern Pacific & Hawaii	1983-1984
ABLE-2A	Amazon Rain Forest, Dry Season	1985
CITE-2	Eastern Pacific, Moffett Field, CA	1986
ABLE-2B	Amazon Rain Forest, Wet Season	1987
ABLE-3A	Northern Latitudes, Alaska	1988
CITE-3	Eastern Atlantic, Wallops, VA & Natal, Brazil	1989
ABLE-3B	Northern Latitudes, Canada	1990
PEM-West A	North Western Pacific, Fall	1991
TRACE-A	Tropical Atlantic	1992
PEM-West B	North Western Pacific, Spring	1994

The archives from the ABLE-3A, ABLE-3B, PEM-West A, and TRACE-A have been completely reformatted and submitted to the DAAC system for review and installation. These data include the airborne measurements and ground measurements, where applicable, as well as ancillary measurements such as trajectory plots, satellite images, ozonesonde, and rawindsonde data. The archive for the PEM-West B mission will be submitted to the DAAC in September, 1995. The archived data for the remaining missions require extensive reformatting prior to acceptance by the DAAC system. Currently reformatting of the ABLE-2A and ABLE-2B is underway. The ABLE-2 missions should be completed by the end of 1995. Reformatting of the remaining archives listed above will follow starting with the CITE-3 mission and ending with the ABLE-1 mission. It is anticipated that the reformatting of these data will continue through calendar year 1996. Information concerning any of the GTE mission archives, as well as the archived data, can be obtained through the GTE Project Office by sending an e-mail request to gte_archive@larc.nasa.gov.

Publications

None

Augmentation of Field Operations for the NASA Pacific Exploratory Mission (PEM-West)

Investigator

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Research Objectives

This task provides additional funding to support the field deployment of the DC-8 aircraft during the PEM-West (B) study.

Summary of Progress and Results

The PEM-West mission was designed to study the impact of outflow from the Asian continent on the troposphere over northwestern Pacific region. Phase A of PEM-West was conducted during September-October, 1991; Phase B was conducted in the March-April, 1994. These two time periods were selected to provide a contrast between periods of minimum outflow (i.e., Fall) and periods of maximum outflow (i.e., Spring). During PEM-West (B) a transit flight from Hong Kong to Japan, was specifically designed to fly parallel and downwind of the major commercial air traffic corridor between Hong Kong and Japan. The objective of this flight was to determine if NO_x emissions associated with the corridor and/or individual aircraft could be observed. To date analysis of measurements obtained during this flight show clear evidence of aircraft emissions which appear to be associated with individual aircraft, but no obvious enhancement of the "background" NO_x (or NO_y) associated with a "corridor-effect." Complicating the effort to quantify the various sources of NO_x for this flight, as well as for other flights during PEM-West, is the additional results from the PEM-West study demonstrating that lighting, as well as continental outflow, can be major sources of NO_x in the northwestern Pacific region.

Publications

Papers describing results from the PEM-West (A) are being reviewed for inclusion in a special section in *Journal of Geophysical Research-Atmospheres*. The PEM-West (A) archive is available through the Langley DAAC or by request at gte_archive@larc.nasa.gov.

Manuscripts describing results from the PEM-West (B) are being prepared and will be submitted September, 1995 for publication in *Journal of Geophysical Research-Atmospheres*. The PEM-West (B) archive will be available September 1, 1995.

Measurements of Ice Nucleating Aerosols in the Upper Troposphere and Lower Stratosphere

Investigators

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Research Objectives

Our contribution to the SASS project focuses on developing and utilizing a new ice nuclei (IN) detector: the continuous flow diffusion (CFD) chamber. The CFD will be deployed on the NASA DC-8 aircraft to measure the ice nucleating properties of aerosols at high altitudes, including number concentration active at particular temperatures and ice supersaturations. In addition, the CFD is configured to separate ice nuclei from the total aerosol sample; we are developing techniques for the collection and characterization of both aerosol fractions to determine their size and composition. Since IN are present in low abundances, single-particle electron microscopy (EM) techniques will primarily be used for this purpose. A comparison will be made of the characteristics of IN and non-IN, in and outside of contrails, to assess whether aircraft emissions significantly affect IN abundance, and whether a distinct chemical signature for such perturbations is observed.

Summary of Progress and Results

During year one, our efforts have been focused in two major areas: 1) continued development of hardware and software components of the airborne version of the CFD, and 2) development of the aerosol and crystal collection and chemical characterization techniques.

(1) An experimental version of the new refrigeration system for the airborne CFD has been assembled and is now undergoing experimental tests. Initial results show that this system can reach -40°C with uniform wall temperature. Calculations of particle nucleation and growth in the CFD have been performed for a range of chamber dimensions and air flow rates, and will be used to size the airborne chamber. Development continues on software for the aircraft instrument system. This software will provide for instrument control, real-time display, and data recording for the airborne version of the CFD.

(2) We are currently designing proof-of-concept experiments to demonstrate the ability of the CFD and impaction technique to isolate and characterize ice nucleating aerosols. The prototype CFD is being used as a laboratory instrument for these studies. Mr. Yalei Chen, the Ph.D. level graduate student who will be responsible for the single particle electron microscopy analyses, has been developing techniques for generation of test aerosols; has completed training and certification on the CSU scanning and transmission electron microscopes; and has performed EM analyses of our first samples from the proof-of-concept experiments. Computer/video image capture hardware and image analysis software has been acquired for processing of microscope data. Additional tasks currently being worked on include determining the best choice of substrate for crystal collection, and calibration of the optical crystal detector with aerosols of known size, shape, and composition.

Publications

The following papers were presented at the Annual AEAP Meeting in Virginia Beach, VA, 23-28 April 1995:

Rogers, D. C., P. J. DeMott, Y. Chen, and S. M. Kreidenweis, Ice nucleating aerosols: Plans for high altitude measurements and chemical characterization.

DeMott, P. J., D. C. Rogers, and S. M. Kreidenweis, Susceptibility of ice formation in upper tropospheric clouds to the quantity and size of insoluble components in mixed-aerosols.

Analysis of Existing Odd Nitrogen Data for Emission Effect of Subsonics

Investigators

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Research Objectives

Utilize existing datasets to examine the effect of subsonic aircraft emissions on the odd nitrogen (NO_y) distribution in the atmosphere.

Summary of Progress and Results

An analysis of the data obtained during the AASE II was made to characterize small scale increases (spikes) of reactive nitrogen species with mixing ratio greater than 0.1 pptv. By using the NO_x/NO_y ratio of the spikes as a measure of the age of NO_x after its emission into the atmosphere, the spikes were classified into aged air parcels and fresh emissions. Further classification of the air parcel was made by examining the correlation between NO_y and other trace species including tracers of various NO_x sources.

We found that the majority (60%) of a total of 236 NO_y spikes were due to the mixing of air masses with different degrees of stratospheric influence. Spikes due to aircraft emissions were the second most abundant (30%). As expected, the probability of finding aircraft emissions increased with the magnitude of the NO_y spikes. The origin of most of the rest spikes could not be determined with certainty. Contribution by near surface sources and by lightning was found to be less than 5 percent, apparently due to the winter season and emphasis on high latitudes in the AASE II experiment.

Publications

Zheng, J., A. J. Weinheimer, B. A. Ridley, S. C. Liu, G. W. Sachse, B. E. Anderson, and J. E. Collins, Jr., An analysis of aircraft exhaust plumes from accidental encounters, *Geophys. Res. Lett.*, *21*, 2579-2582, 1994.

Contrail-Cirrus Studies at FARS

Investigator

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Research Objectives

To use data from ground-based remote sensors at the Facility for Atmospheric Remote Sensing (FARS) to study the local frequency of occurrence and the physical, microphysical and radiative properties of contrails. Research components include retrospective analyses of an eight-year cirrus dataset collected in support of Project FIRE, new advanced scanning polarization lidar and 95 GHz Doppler radar measurements of evolving contrails, and persisting contrail case study research to assist in satellite contrail identification/validation research with NASA co-investigators.

Summary of Progress and Results

Examination of our ~1750-hour Project FIRE cirrus cloud dataset is revealing a number of interesting contrail features. Contrails are identified in ~20% of all supporting all-sky photographs (~35% in the spring and fall seasons), demonstrating the effects of the heavy local jet air traffic. Using lidar height and local radiosonde data, contrails persist only below -40 degrees C (where ice forms homogeneously from droplets), but can persist at relative humidities of >85% (with respect to ice). New contrails are strongly scattering in the visible and have relatively brief but significant effects on the surface radiation budget; only aged contrails with significant vertical development are active in the infrared. Although on the basis of corona displays and recent *in situ* data (during the April 1994 RCS IOP at the Southern Great Plains CART site) contrails are often composed of high concentrations of minute (10-30 microns) ice particles, at other times they generate halos and arcs, and so contain larger (>100 microns) pristine ice crystals. Extended observations with little or no "natural" cirrus present show that the spreading of a series of contrails can generate extensive cirrostratus layers. Subvisual contrail fields have also been observed. Datasets for satellite studies (with P. Minnis) have been collected.

Publications

Sassen, K., The properties of contrails: Toward an assessment of climate change potential, Conference Cloud Physics, Dallas, TX, AMS Preprints, 407-412, 1995.

Sassen, K., R. Benson, and K. Duffy, Contrail studies at FARS: Evaluation of potential for climate change, 17th International Laser Radar Conference, Sendi, Japan, Abstracts, 552-553, 1994.

Contrail Optical and Infrared Parameters from High Altitude Aircraft Observations

Investigators

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Research Objectives

Remote sensing observations of contrails from the NASA ER-2 high altitude aircraft were acquired in the 1991 and 1986 FIRE cirrus experiments. The observations involve multi channel, high spatial resolution visible and infrared imaging of contrails. In addition height structure was obtained with the ER-2 Cloud Lidar System. Several cases have been found where significant numbers of contrails are present in the existing observations. The contrails are thought to result primarily from *in situ* cloud physics aircraft that were part of the FIRE missions. The contrail observations are investigated for three objectives. First, microphysical properties and radiation parameters of the contrail cirrus are derived from analysis of the multispectral reflected and emitted radiation and the lidar height structure. The retrievals are contrasted with the surrounding non contrail cirrus. Second, the ability to detect contrails in satellite data is studied by averaging the high spatial resolution contrail images to the spatial resolution of satellite data such as AVHRR imaging. The ability to detect the contrail presence in the satellite resolution image is determined. Third, the overall fraction of cloud forcing for the observed cirrus scene due to the presence of the contrails is estimated.

Summary of Progress and Results

Initial results and conclusions from the study have been completed. There are the following preliminary conclusions for contrail microphysics and evolution from the remote sensing:

- Multispectral visible/infrared imaging and lidar analysis can usefully estimate contrail microphysics and radiative parameters and their evolution.

- New contrails are composed of equivalent sphere ice particles of less than 5 mm size and with observable growth.

- Contrail liquid water content is on the order of that of surrounding natural cirrus - jet exhaust is an insignificant component.

For the radiative effects and satellite detectability of contrails the preliminary conclusions are:

- Of the analyzed contrail cirrus, replacement of contrails by surrounding cirrus changed overall visible and infrared radiances by several per cent.

- The older contrails indicated the least perturbation per unit area but gave the greatest influence when the overall aerial extent was considered.

- The new contrails were much more detectable at satellite resolution due to greater brightness and split window contrast than old contrails. Analysis of the radiation effects of contrails and based on a single case study at present. A paper for publication is in preparation.

Publications

Only conference presentations at the current time have been completed.

Aircraft Submillimeterwave Measurements

Investigator

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Research Objectives

The objective of this effort is to contribute a remote sensing vertical profiling capability for upper tropospheric and lower stratospheric H_2O, O_3, HNO_3, N_2O, ClO and HCl to complement the measurements of *in situ* instrumentation on the NASA ER-2 and future remotely piloted high altitude aircraft.

Summary of Progress and Results

The submillimeterwave mixer for the ~400 GHz radiometer for upper trop/lower stratospheric H_2O measurements has been procured. Discussions with Ames and Lockheed personnel are continuing to define the details of the accommodation of the SLS instrument in the ER-2 super pod. We expect to have a final configuration in April 1995 and then complete the layout drawings for the SLS instrument as modified to fit in the super pod.

Publications

None

DC-8 Scanning Backscatter Lidar

Investigators

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Research Objectives

This task is for development of an airborne backscatter lidar/radiometric instrument suite, consisting mostly of existing sensor systems installed on the NASA DC-8 or other appropriate aircraft with an elevation scanning capability. A scanning mirror pod attached to the DC-8 aircraft will provide for scanning lidar observations ahead of the DC-8 and fixed-angle upward or downward observations. The lidar system installed within the DC-8 will transmit 272 mJ at 1.06 and 0.53 μm simultaneously. Range-resolved aerosol backscatter will be analyzed in terms of cloud/contrail spatial distributions and two-wavelength analysis of mean particle sizes.

The objectives of the project are:

- Map contrail/cloud vertical distributions ahead of DC-8.

- Provide DC-8 guidance into enhanced scattering layers.

- Document DC-8 flight path intersection of contrail and cloud geometries.

    - *In situ* measurement positions relative to cloud/contrail shape

    - Extension of *in situ* measurements into the vertical (integrated contrail/cloud properties)

- Analyze contrail/cloud radiative properties with LIRAD (combined lidar and radiometry) technique. (We assume NASA will instrument the DC-8 with an upward-viewing narrow-beam infrared radiometer.)

- Evaluate mean particle sizes of aircraft emissions from two-wavelength observations.

- Study contrail/cloud interactions, diffusion, and mass decay/growth.

The scanning mirror pod may also provide a scanning capability for other remote sensing instruments including the SRI ozone lidar and FTIR spectrometer.

Summary of Progress and Results

Work has just begun on this task so it is too soon to report any progress.

Publications

None

ALIAS Measurements of CO, CH₄ and N₂O in Support of SASS

Investigators

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Research Objectives

One research component of the Subsonic Assessment (SASS) program includes dedicated field campaigns with an emphasis on studying the atmospheric region within a few kilometers of the tropopause. Prior to this effort, it was recognized that flights of the ER-2 aircraft during the 1994 ASHOE/MAESA campaign offered an opportunity to collect data over a wide latitude range which would be relevant to the SASS objectives, especially data from the aircraft ascent and descent profiles. In providing funding for a post-doc for one year, this task was directed to producing and studying the ALIAS measurements of CO, CH₄ and N₂O collected during ASHOE/MAESA with an emphasis on the aircraft ascent/descent and dive regions.

Summary of Progress and Results

Under the AEAP/SASS "fast-payback" funding for FY94, Dr. Hua Hu was hired in February 1994 to assist with the ALIAS-I data processing and interpretation during the 1994 ASHOE/ MAESA campaign, with a particular emphasis on AEAP/SASS needs. In this campaign, three measurements of the fundamental tracer N₂O were made, and much effort was put into examining data quality and providing intercomparison plots to unravel apparently systematic differences in the three N₂O data bases, especially in regions of high N₂O amounts close to the tropopause regions of concern to SASS.

For ASHOE/MAESA, the ALIAS instrument added to the ER-2 aircraft payload the new capability of measuring CO. By flushing the ALIAS fore optics to remove any possibility of tropospheric sampling memory, an extensive data base in CO over a wide range of latitudes was collected from the mission. A clear gradient in the tropospheric mixing ratio of CO is observed from northern to southern latitudes, with a value about 3 times smaller in New Zealand than in California. In the lower stratosphere (10-15 km), the CO data show wide variability, and a seasonal contribution, with a measured mixing ratio dependent on the history of the air parcel temperature. Sources and sinks of CO in the stratosphere are also under investigation, as well as the downwelling and upwelling processes in the polar vortex and tropical regions, respectively.

Publications

Hu, H., C. R. Webster, R. D. May, D. C. Scott, R. J. Salawitch, P. O. Wennberg, D. W. Fahey, E. Woodbridge, and M. H. Proffitt, Airborne *In-situ* measurements of carbon monoxide in the upper troposphere and the lower stratosphere, in preparation, *J. Geophys. Res.*

Measurement of Subsonic Turbine Engine Exhaust Emission Characteristics in an Altitude Ground Test Facility

Investigators

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Research Objectives

The primary objectives of this work element are to perform exit plane engine exhaust gaseous and particulate emissions measurements at sea-level static and simulated altitude flight conditions to:

* obtain representative exhaust emissions at altitude cruise flight condition(s),

* compare non-intrusive and extractive gas sampling techniques, and

* support extrapolation technique studies and development.

As SASS analysis tools are developed and critical research activities completed, vital parts of the assessment rely upon accurate emissions measurements from a cross-section of engine types at cruise flight conditions. Dedicated simulated-altitude test programs would exceed current available funds; therefore, "piggy-back" measurements on existing test programs provide a viable means for NASA to achieve required engine emissions data. Since sea-level data is more easily obtainable, development or validation of extrapolation techniques for utilization of sea-level static data for flight emissions determination is important to a long-term comprehensive atmospheric assessment of turbine engines. This effort provides an excellent for comparisons of selected non-intrusive and more conventional extractive gas sampling techniques.

Summary of Progress and Results

This work is managed through NASA Lewis by Dr. Richard Niedzwiecki. The objectives of this work element rely upon the teaming of Arnold Engineering Development Center (AEDC), Aerodyne Research Incorporated (ARI), the University of Missouri-Rolla (UMR), the engine test program sponsor(s), and the engine manufacturer(s). The work was initiated in December of 1994 with the establishment of objectives and development of a detailed work plan. Engine test facility hardware interface components have been designed and fabricated for installation of the diagnostic instrumentation. A cruciform rake equipped with gas sampling probes, mach flow angularity probes, and total temperature probes has been developed and tested in a similar flow-field environment allowing preliminary measurements at sea-level static conditions in an altitude test facility. Aerodynamic probe data provide static temperature and static pressure profiles required for analysis of the optical line-of-sight data. Presently, that data will be analyzed and preparations are underway for a full set of measurements later in the year.

Publications

None

Chemical Processes in the Turbine and Exhaust Nozzle

Investigators

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Research Objectives

Accurate determination of trace species in engine exhaust is critical for meaningful assessment of the atmospheric effects of both current and future aircraft. Chemical processes inside the combustor and downstream of the engine exit plane have been the focus of a number of studies. In comparison, little inquiry has been directed at processes occurring in the turbine and nozzle. The objective of this effort is to gain an understanding of the evolution of primary pollutants, trace species, and aerosols as exhaust travels through the turbine and nozzle.

The approach used in this investigation consists of the development of a numerical tool combining the calculation of both chemical and fluid processes. The fluid-chemistry coupling is assumed to be a one-way interaction in which fluid processes govern the chemical evolution. Parametric investigations regarding the relevance of specific flow-field characteristics (i.e. turbulence, boundary layer interactions, non-uniformities, coolant flows, etc.) as well as the role of differing input and boundary conditions (i.e. wall effects, nonuniformity and nonequilibrium concentrations at the combustor exit, etc.) will be conducted to isolate the important processes affecting trace species evolution. Both mean and unsteady flow conditions will be investigated.

Longer-term goals include the calculation of multiple stages in the turbine, and eventual connection with models of combustor dynamics as well as with plume and wake fluid chemical calculations leading to atmospheric deposition. This tool could potentially provide an alternative to expensive full-scale engine tests and perhaps an earlier assessment of emissions from developmental engines.

Summary of Progress and Results

This investigation is currently six months into a three year program. Several possible numerical approaches have been identified. These include: 1) post-processing of the chemistry based on a given computational solution, 2) a reduction in stiffness of the chemical system through approximations to the full chemical scheme, 3) direct calculation to provide full resolution of chemical time scales, and 4) either an explicit or implicit operator-splitting scheme in which, respectively, the chemistry is calculated one time step after or at the same time as the fluid iteration. The first attempt at numerical interaction will be based on an explicit operator-splitting scheme in which the chemistry is calculated using endpoints given by a larger fluid iteration time step.

The tool is based on the full 3-D, Reynolds averaged Navier-Stokes internal flow code, NEWT, developed by Professor W. N. Dawes at the Whittle Lab, Cambridge University, Cambridge, UK. This code is currently being expanded to calculate species equations. Initial calculations will be based on constant Schmidt numbers and the chemistry will be calculated based on mean concentrations.

Assessment of the need to include turbulent effects within the reaction mechanism will be made later. The code will be validated through comparison with known solutions.

Initial 1-D investigations using assigned, representative temperature and pressure profiles are underway to provide some preliminary indications as to the validity of the numerical approach. A chemical reaction set based on the H-N-C-O elements has been selected for this initial approximation. In this suite of runs, general observations regarding the range of expected mole fraction changes, as well as a deeper understanding of the distribution of chemical time scales are sought. The sensitivity of the chemical scheme to flow temperature perturbations as well as the effect of various approximations to the temperature history are also investigated. Future calculations using this 1-D model will include streamline profiles selected from turbine CFD solutions using NEWT, as well as full subsonic engine temperature and pressure profiles derived from representative subsonic engine cycle decks under development by other members of the AEAP.

Publications

None

Laboratory Studies of Sulfate Aerosol Chemistry as Related to Tropospheric Composition

Investigator

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Research Objectives

The objectives of this research are to study the interactions of a number of key atmospheric constituents (N_2O_5, NO_3, HO_2 and OH) with surfaces characteristic of atmospheric particulate matter. Particular emphasis is being given to studying these interactions with $(NH_4)_2SO_4$/ H_2SO_4/H_2O ternary mixtures, a chemical system prototypical of upper tropospheric aerosol composition.

Summary of Progress and Results

Since the start of this project six months ago, research has been focused in two directions. First, the heterogeneous interactions of the OH radical have been studied on a variety of surfaces coating the inner walls of a low temperature flow tube using resonance fluorescence as the OH detection technique. Preliminary results indicate that:

- OH has a reaction probability close to unity on sulfuric acid surfaces of 40 to 60 wt% composition at 230 K. The irreversible loss of OH is most likely due to the reaction between OH and $H_2SO_4^-$.

- Although somewhat nonreactive on bare ice surfaces, OH exhibits a pronounced reactivity with ice surfaces which have adsorbed molecules such as HCl, HNO_3 and 1-hexanol.

Second, we are nearing the completion of an aerosol kinetics experiment where the reactions of N_2O_5 will be studied on tropospheric aerosols. A chemical ionization source for a differentially pumped mass spectrometer has been built for the detection of N_2O_5 in the presence of HNO_3. Detection limits on the order of 10^{11} molecules/cm^3 from atmospheric pressure are currently being obtained. In order to determine aerosol surface areas in the flow tube, NH_4HSO_4 aerosols (65 wt% composition, 2-micron diameter) are being sized with a right-angle-scattering optical particle counter with an upper concentration limit of 10^4 to 10^5 particles/cm^3.

Publications

None

Reaction Kinetics in Condensed Phase Near the Tropopause

Investigators

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Research Objectives

Our objective is to measure homogeneous condensed-phase reaction rate constants and quantum yields which may be important in aerosol particles near the tropopause. Chemical reactions involving aerosol particles are of considerable interest, since their surfaces may be important in chemical reactions related to ozone depletion and the Polar Stratospheric Ozone Holes, but little is known about the homogeneous solution phase reactions at very low temperature and with high sulfuric acid content. The subsonic aircraft fleet may perturb the atmosphere near the tropopause where the aerosol particles probably are similar to the highly concentrated sulfuric acid aerosols found in the lower stratosphere. The reactions proposed for study involve photolytic production of free radicals and their subsequent reactions in concentrated sulfuric acid solutions. The effects of temperature, acid content, and total ionic strength are being investigated, since all three of these parameters significantly affect rate coefficients and (possibly) quantum yields for free radical production.

Summary of Progress and Results

During the time since this project began in July, we have purchased a high quality water purification system and have assembled the necessary laboratory equipment. The experiment utilizes a pulsed excimer laser operating at 248 nm to generate free radicals which are monitored by time-resolved absorbency in a 16-pass White cell arrangement. Currently, we are investigating reactions of the sulfate radical anion with itself and with persulfate di-anion, the radical photolytic precursor. We are using these first experiments to refine our experimental techniques and to address a controversy in the literature. After we finish investigating the effects of ionic strength and sulfuric acid content on these reactions at 295 K, we will investigate lower temperatures. We plan to investigate several aqueous reactions involving OH, nitrate, and sulfate radicals.

Publications

None

Quenching Effects in Laser Detection of Atmospheric OH and HO_2

Investigator

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Research Objectives

Emissions from aircraft flying high in the troposphere and low in the stratosphere have the potential of modifying those regions of the atmosphere. Of particular concern is the possible influence of NO_x, CO, and hydrocarbons on the concentrations of ozone in the these regions. The OH and HO_2 radicals are central to the chemical reactions and cycles that determine ozone concentrations in the lower stratosphere and upper troposphere. Knowing their concentrations is not only of direct importance to evaluating these questions, but constitutes an especially stringent test of our knowledge of the chemistry of these regions. Measurements of these radicals has been made using laser-induced fluorescence (LIF) in the Harvard instrument aboard the ER-2. This instrument is calibrated on the ground in a nitrogen atmosphere but flown in air at colder temperatures. The data analysis must include the effects of quenching and vibrational energy transfer (VET), which determine the fluorescence quantum yield. These collisional processes have rates that vary with temperature, as studied earlier under support from GTE (quenching) and from HSRP (VET); the temperature has a significant influence on the quantum yield. Furthermore, the HSRP-sponsored studies showed that VET produced an excited, nonthermal rotational distribution in the transferred molecules. Quenching of these high J levels and its temperature dependence will be studied in the present project. OH will be produced in high J levels of the ground state by photolysis of HNO_3, and their quenching studied by LIF decay curves in a low pressure cooled cell. A quantum state specific model of the relaxation, providing the overall quantum yield as a function of temperature will be assembled.

Summary of Progress and Results

This project began in December 1994 and no significant work has taken place to date (early 1995).

Publications

None

Chemistry of Hydrocarbon Species Relevant to Subsonic Aircraft

Investigator

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Research Objectives

This task is intended to provide fundamental laboratory data on the rates and mechanisms of key elementary photochemical reactions that relate to the processing of non-methane hydrocarbons in the upper troposphere. Formaldehyde and ethylene are among the major non-methane aircraft effluents to be studied. In addition we will investigate photochemical aspects of propane oxidation that relate to the formation of peroxyacetyl nitrate, a significant reservoir of tropospheric nitrogen.

Summary of Progress and Results

Initial results have been obtained for the OH-induced oxidation of ethylene. One cm^{-1} resolution infrared spectra have been obtained for mixtures of OH, ethylene, and O_2 and are being analyzed. A product peak is observed at approximately 1750 cm^{-1} which suggests formation of a carbonyl containing product. Analysis of the spectra is continuing and studies of the ethylene/OH/O_2/NO system are planned.

An apparatus design has been developed for studies of the formaldehyde reaction with HO_2. The apparatus will utilize an excimer laser to initiate production of HO_2 and an near-infrared diode laser for detection of the HO_2. Diode lasers operating at 1.3 microns have been obtained and characterized.

Publications

None

An Investigation of Cirriform Cloud Microphysics: Laboratory Measurements to Aid Parameterization Development

Investigator

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Research Objectives

This study seeks to reduce uncertainties in knowledge about ice crystal formation in the upper troposphere. We are developing an experimental system capable of forming and growing individual ice crystals under well defined conditions that duplicate those found in cirriform clouds. In order that the laboratory simulation be valid, it is important that the crystals be grown under free-fall conditions. This capability is to be accomplished by coupling a vertical wind tunnel to an electrodynamic levitation cell in a configuration that minimizes the influence of chamber walls. The ice phase will be initiated within representative solution droplets that are held in place against the updraft by electrodynamic forces in the cell. The subsequent growth of the ice particle by vapor deposition will take place during suspension by a vertical current of air of controlled temperature, pressure, and supersaturation. The extended objective of this project is to use the laboratory data to test various physically based crystal growth models, from which microphysical parameterizations can be developed for use in cloud models. This hierarchical approach offers an effective means for developing reliable and robust numerical models with which to assess the impacts of jet aircraft on the climate and chemistry of the atmosphere.

Summary of Progress and Results

The development of an experimental capability to grow ice crystals under realistic low-temperature conditions requires consideration of a severe set of criteria. An early emphasis in this project has therefore been to establish a clear set of design specifications, followed by suitable laboratory testing to validate some of the more uncertain design features. Prototype testing has already validated the use of ring electrodes for levitating the initial solution droplets, and we have achieved long-term (> one hour) suspension of surrogate particles in a simple wind tunnel. The precise generation of supersaturations in the air stream and its preservation in the chamber up to contact with the growing ice particle require additional flow tests before the design of the experimental system can be finalized. In parallel with the laboratory work, we have succeeded in extending the range of applicability of the crystal growth model that will later be tested against the experimental data.

Publications

Lamb, D., and J. P. Chen, An expanded parameterization of the growth of ice crystals by vapor deposition, Conference Cloud Physics, Dallas, TX, AMS Preprints, 389-392, 1995.

Laser Laboratory Spectroscopy in Support of STRAT

Investigators

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Research Objectives

Interpretation of atmospheric spectra requires accurate knowledge of molecular line parameters including absorption intensities, air-broadening coefficients, and their dependence on temperature. The research carried out under this task will provide laboratory measurements of molecular line parameters for selected species observed in ATMOS and balloon spectra of the stratosphere (HNO_4, CF_4), and for a near-infrared band of water vapor (1.37 microns) that will be used for atmospheric monitoring by a new class of recently-developed diode laser spectrometers.

Summary of Progress and Results

Svante Höjer arrived in August 1994 to begin work on laboratory spectroscopic studies in support of SASS. During the initial eight months of work on this task IR studies of peroxynitric acid (HNO_4) near 1397 cm^{-1} have been completed. Other than the strong band at 803 cm^{-1} previously observed in ATMOS spectra, the 1397 cm^{-1} band is the only other absorption band of HNO_4 that could potentially be observed in atmospheric spectra. Room temperature and low temperature (220 K) diode laser spectra were recorded of the 1397 cm^{-1} band of HNO_4, and air-broadening coefficients were obtained for use in analysis of balloon and ATMOS Fourier transform spectra. In collaboration with Charles Miller (a post-doc working with Stan Sander at JPL) a high-resolution Fourier transform spectrum of the HNO_4 1397 cm^{-1} band was also recorded. This spectrum is the first high-resolution spectrum of the HNO_4 1397 cm^{-1} band to be recorded. Analysis yielded absorption coefficients at 220 K suitable for analysis of atmospheric spectra. A manuscript has been submitted to the *Journal of Quantitative Spectroscopy and Radiative Transfer*.

In addition to the HNO_4 work, Dr. Höjer has been investigating the possibility of using fiber optics to transfer diode laser beams instead of independent banks of steering mirrors. There are two primary goals to this work. First, it must be determined whether or not the output beam from the fiber can be shaped sufficiently well (using inexpensive collimators) to provide a beam profile adequate for injection into a multipass Herriott cell. Secondly, if proper beam shaping can be accomplished, sensitivity studies must be carried out to determine the level of optical fringing that will result from reflections in the laser-to-fiber, and fiber-to-Herriott cell interfaces. If these studies are successful it will be possible to guarantee optical alignment in both near-IR (1-2 μm) and mid-IR (3-10 μm) aircraft instruments by elimination of alignment drifts due to temperature drifts in the steering mirror mounts.

Currently, laboratory measurements are being made of line strengths and air-broadening coefficients for CF_4 (1283 cm^{-1}), and line strengths and air-broadening coefficients for H_2O (from 200 K to 300 K) needed for analysis of planned atmospheric measurements in the 1.37 μm region.

Publications

Höjer, S., R. D. May, and C. E. Miller, Intensities of the 1397 cm^{-1} band of HO_2NO_2 and feasibility of atmospheric detection, submitted to *J. Quantitative Spectroscopy and Radiative Transfer*, 1995.

Höjer, S., and R. D. May, Absorption sensitivity limitations in fiber-coupled multipass absorption cells, in preparation, *Applied Optics*.

Laboratory Studies of Nitric Acid Hydrate Aerosols: Formation and Characterization

Investigators

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Research Objectives

Polar stratospheric clouds have now been conclusively implicated in the ozone destruction mechanism that leads to the formation of the Antarctic Ozone Hole and the goal of our present research program is to obtain a better understanding of the microphysics and chemistry associated with these aerosols through laboratory studies.

Summary of Progress and Results

In the first year of this grant we have made considerable progress towards realizing our research objective. First we have developed and constructed the equipment needed to carry out the studies of the optical properties of laboratory generated aerosols. In the process of recording FTIR spectra of many of these aerosols we developed a new approach for determining refractive index data directly from the aerosol. The method was developed using water ice aerosols. The method was shown to be reliable and extremely flexible, allowing us to determine the temperature dependence of the real and imaginary components over a wide range, including the first direct measurements at stratospheric temperatures. This work has now been extended to nitric acid trihydrate (NAT) and nitric acid dihydrate (NAD). Our results differ somewhat from the results obtained from thin film studies, which we interpret as being due to the fact that the aerosols are much more crystalline than the films. These differences have important implications for modeling and remote sensing of these species in the stratosphere.

The role of sulfuric acid particles in the formation of NAT and in more global ozone depletion is also of great current interest. We are therefore in the process of extending these studies to the ternary sulfuric acid/ nitric acid / water systems. In addition to the determination of optical properties we are interested in studying phase segregation and freezing in these systems. This will be the focus of the research in the next year.

Publications

Clapp, M. L., D. R. Worsnop, and R. E. Miller, Frequency dependent optical constants of water ice obtained directly from aerosol extinction spectra, in press, *J. Phys. Chem.*, 1995.

Richwine, L. J., M. L. Clapp, R. E. Miller, and D. R. Worsnop, Infrared optical constants of nitric acid trihydrate aerosols, submitted to *J. Geophys. Res. Lett.*, 1995.

Low-Temperature Studies of Atmospheric Chemistry of Nitrogen Oxides

Investigator

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Research Objectives

The purpose of this task is to investigate in the laboratory reactions of nitrogen oxides of atmospheric importance, under temperature and pressure conditions applicable to the lower stratosphere and upper troposphere.

Summary of Progress and Results

We have carried out chemical kinetics studies using a flow tube which operates in the turbulent flow regime, and which is coupled to a chemical ionization mass spectrometer. The flow tube and the chemical ionization sections of the apparatus operate at pressures between about 50 and 760 Torr, and at temperatures down to 180 K.

We measured the rate constant for the $HO_2 + NO$ reaction by monitoring directly the decay of HO_2 and the appearance of OH at pressures between 70 and 200 Torr. The reagent ions employed for chemical ionization were generated by flowing trace amounts of SF_6 or of NF_3 through a corona discharge. The rate constant was found to increase by approximately 50 percent as the temperature was lowered from 300 K to 200 K. Our results are in very good agreement with those reported by Howard in 1979, indicating that the rate constant does not have a substantial pressure dependency at atmospherically relevant temperatures.

Publications

Seeley, J. V., R. F. Meads, M. J. Elrod, and M. J. Molina, Temperature and pressure dependence for the $HO_2 + NO$ reaction, submitted to *J. Phys. Chem.*, 1995.

Hydroperoxy (HO2) Radical Spectroscopy and Kinetics Relevant to the Effects of Subsonic Aircraft Emissions on Lower Stratospheric Ozone

Investigators

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Research Objectives

The NASA research efforts since the start of this grant (6/94) have been in the following three directions: 1) design/construction of a cooled flow cell for time resolved IR laser study of $OH/HO_2/O_3$ chemical kinetics; 2) design, construction and testing of slit Corona discharge sources for jet cooled spectroscopy of HO_2 radicals; and 3) a reanalysis of the Einstein A coefficient for $O_2(a^1\Delta_g)$ --> $O_2(X^3\Sigma_g)$, which indicates a radiative decay rate of $1.47 \times 10^4 \, s^{-1}$. This is a factor 1.75 smaller than the value used almost exclusively in the aeronomy field for the past 30 years, and impacts directly on ozone concentrations inferred from satellite based measurements of $O_2(a^1\Delta_g)$ airglow.

Summary of Progress and Results

Achievements under the NASA grant have been made in the following three areas: 1) design and construction of a temperature controllable flow cell for $OH/HO_2/O_3$ kinetics; 2) development of pulsed slit Corona discharge sources for efficient production and supersonic cooling of HO_2 radicals; and 3) theoretical analysis of $O_2(a^1\Delta_g)$ radiative lifetimes relevant to ozone concentration studies from satellite airglow measurements. Each of these is amplified below.

- The first stage of the project is to detect HO_2 radicals in the 1.3-1.5 µm overtone region under supersonic expansion conditions. To this end, we have already developed novel continuous wave (cw) methods for tunable difference frequency mixing single mode Nd:YAG and dye lasers to scan over the full 1.1-2.0 µm region. The system currently is scanned under computer control at spectral resolution of better than 0.0002 cm^{-1}.

  There has been significant progress toward developing a pulsed slit Corona discharge source for supersonically cooled radicals in the high-resolution slit jet spectrometer. Though Corona discharges have been widely used for pinhole geometries, both with pulsed and cw expansions, there has been no report in the literature of any pulsed slit discharge source. However, the long path length advantage and Doppler velocity compression of the slit nozzle geometry is crucial for obtaining a sufficient level of direct absorption sensitivity to detect HO_2 with high S/N. We have succeeded in modifying the pulsed slit nozzle previously developed in our labs to generate a pulsed discharge across the dense region of the expansion. The circuitry for high voltage modulation of the discharge has been assembled and tested. We have tried several designs and geometries, and find that the most promising is with a discharge directly across the defining jaws of the slit aperture. The key issue is maintaining a relatively uniform discharge in the presence of significant gas and density gradients. This problem is solved by a longer expansion channel and higher voltages with correspondingly higher ballast resistance to stabilize the discharge. A version that meets this criterion is currently being built in the instrument shops and should be available for testing within a few weeks.

- The second phase of the project involves kinetic measurement of $OH/HO_2/O_3$ radical chain reactions at temperatures relevant to the upper troposphere/lower stratosphere. This involves the combination of three devices: 1) a temperature regulatable flow cell from 180 K to room

temperature; 2) an excimer photolysis laser for pulsed generation of the chain initiating OH radicals; and 3) a tunable IR laser source in the OH v=1-0 region, which is currently a Kr^+ pumped, single mode F-center laser from an AFOSR project. The flow cell has already been constructed, with evacuated regions for preventing condensation of room moisture on the entrance and exit windows. The closed-cycle cooling system has been purchased and installed, with sufficiently strong circulation pumps to achieve operation down to the necessary 180 K temperatures. We next need to modify the present glass vacuum rack for mixing and delivery of O_3/HNO_3 reagents to the flow cell. This will be done while the AFOSR project currently using the F-center laser is brought to an appropriate stopping point (within the month).

While both Corona discharge and flash kinetic apparatuses have been in a process of being designed and constructed, we have directed our attentions to other issues of relevance to NASA in atmospheric modeling. Specifically, in collaboration with Dr. Martin Mlynczak at NASA Langley Research Center, we have investigated the $O_2(a^1\Delta_g)$ --> $O_2(X^3\Sigma_g)$ emission system, which is responsible for the oxygen "airglow" features in terrestrial mesosphere and lower thermosphere. The $O_2(a^1\Delta_g)$ is produced mainly as a product of ozone photolysis in the Hartley band, and thus has been widely used to infer ozone concentrations from satellite limb observations (e.g., the Solar Mesosphere Explorer experiment). Analysis of this satellite data requires the radiative lifetime of the upper state, which has been obtained from measured values of integrated band strength and the Einstein relation between B and A. Due to the highly forbidden (g-->g, Δ --> Σ, singlet ---> triplet) nature of the transitions and Bose-Einstein nuclear spin statistics of the identical oxygen atoms, this conversion between B and A is nontrivial. Indeed, we have determined that this has been incorrectly done in the literature, and that a reanalysis of the data yields a radiative decay rate of 1.47×10^4 s^{-1}. This is a factor of 1.75 times smaller than the value of 2.58×10^4 s^{-1} that has been used almost exclusively in the aeronomy field for the past 30 years! This new value for A implies that ozone concentrations (at < 70 km) as inferred from $O_2(a^1\Delta_g)$ airglow must be increased significantly in existing databases. This has been written up and submitted to *Geophysical Research Letters*, where it is currently in press.

Publications

Mlynczak, M. G., and D. J. Nesbitt, The Einstein coefficient for spontaneous emission of the $O_2(a^1\Delta_g)$ state, in press, *Geophys. Res. Lett.*, 1995.

Laboratory Studies of Photodissociation Quantum Yields for Molecules Important in the Lower Stratosphere and Upper Troposphere

Investigators

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Research Objectives

The objective of the above task is to measure quantum yields for the photodissociation of molecules important in the UT/LS. Our work has focused on two molecules, chlorine nitrate ($ClONO_2$) and dichlorine monoxide (Cl_2O). Photodissociation studies using the flash photolysis/ultraviolet absorption technique has shown that broadband irradiation of these molecules in the weak long-wavelength absorption bands leads to pressure-dependent yields. This apparently arises from quenching of metastable excited states formed from efficient intersystem crossing into the triplet manifolds. In the photolysis of Cl_2O, a long-lived structured absorption is seen by time-resolved diode-array spectroscopy which is attributable to a transition originating in one or more of these metastable states.

Summary of Progress and Results

In the last few months, effort has been directed toward the understanding of the observed metastable spectrum in Cl_2O and the electronic structures of the low-lying singlet and triplet states. We have analyzed the Cl_2O metastable spectrum and found that at least two states appear to be contributing to the observed bands. One band has been fully analyzed and the band origin, vibrational frequencies and anharmonicity constants have been determined. The other bands are highly perturbed and cannot be analyzed at the present time. We have also collaborated with two *ab initio* theory groups in the analysis of these spectra. Professor Ian Williams at the University of Bath has obtained vertical excitation energies from the lowest-energy singlet (X1A1) or triplet (1 3B1) states to various excited states. Complete-active-space self-consistent-field (CASSCF) calculations were performed for the two states of lowest energy within each irreducible representation of the C2v point group, for both the singlet and triplet manifolds, using the experimentally determined ground-state molecular geometry. Subsequently the CASSCF molecular orbitals were used in multireference configuration-interaction (MRCI) calculations for the excited states. Additionally, transition dipole moments (and hence oscillator strengths) were determined for both singlet and triplet manifolds. These calculations show that there is an extremely intense transition between the ground triplet (1 3B1) state and the 2 3A2 state for which the vertical excitation energy is about 3.2 eV. This corresponds almost exactly to the energy of the observed metastable spectrum.

The significance of these results is that the observed pressure-dependent yields seen in Cl_2O photolysis at long wavelengths are due to efficient intersystem crossing into metastable triplet states. Cl_2O thus serves as a model for other molecules (of which $ClONO_2$ is a prime example) which may show the same effects. While it is not possible at present to translate these results into atmospheric photolysis lifetimes, it is clear that atmospheric modelers must consider the possibility of pressure-dependent J values for molecules which serve as temporary reservoirs in the lower stratosphere.

Publications

Two publications currently in preparation.

Chemical and Physical Properties of Low Temperature Sulfate Aerosols

Investigator

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Research Objectives

The chemical and physical state of aerosols in the low temperature environment of the upper troposphere/lower stratosphere remains uncertain. The composition and phase of aerosols controls their ability to promote heterogeneous chemical reactions and to serve as cloud condensation nuclei. We are performing laboratory experiments aimed at characterizing the chemical and physical state of sulfate aerosols under low temperature atmospheric conditions.

Summary of Progress and Results

We have used multipass FTIR spectroscopy to study freely-floating sulfuric acid aerosols representative of global stratospheric sulfate aerosols (SSAs). Sub-micrometer sized sulfuric acid (H_2SO_4) particles are generated using a constant output atomizer source. The particles are then exposed to water vapor before being injected into a low temperature cell. Transmission FTIR spectroscopy is used to determine the phase and composition of the aerosols as a function of time for periods of up to 5 hours.

We find that binary H_2SO_4/H_2O aerosols with compositions from 35 to 95 wt% H_2SO_4 remain liquid for over three hours at temperatures ranging from 189 - 240 K. These results suggest that it is very difficult to freeze SSAs via homogeneous nucleation. When attached to a surface, aerosols of similar sizes are observed to crystallize readily. This suggests that H_2SO_4 aerosols containing solid inclusions may be more likely to freeze than pure liquid particles.

Publications

Anthony, S. E., R. T. Tisdale, R. S. Disselkamp, M. A. Tolbert, and J. C. Wilson, FTIR studies of low temperature sulfuric acid aerosols, *Geophys. Res. Lett.,* 22, 1105-1108, 1995.

Heterogeneous Chemistry Related to Subsonic Aircraft Emissions

Investigators

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Research Objectives

Soot particles emitted by the current and projected fleet of subsonic aircraft may impact both the chemistry and radiative properties of the upper troposphere and lower stratosphere by providing nucleation centers for water-based aerosols. We use a low-pressure Knudsen cell reactor to study the uptake of water on soot samples before and after exposure to exhaust and atmospheric gas species. Our goal is to understand the hydration properties of fresh and aged soot particles.

Summary of Progress and Results

We have performed experiments with SO_2, NO_2, O_3, HNO_3 and H_2SO_4 using a commercial carbon black for the soot sample. For the particular soot sample and reactant gas concentrations used here, we see no uptake of water before or after exposure to SO_2, NO_2 and O_3. These results may indicate that these species do not contribute markedly to the conversion of fresh soot particles into condensation nuclei in the wake of an airplane.

The results for HNO_3 and H_2SO_4 are strikingly different. After exposure to these acids, the soot samples readily take up water, indicating a conversion of the soot from hydrophobic to hydrophilic. We are using Fourier-transform infrared spectroscopy to investigate the functional groups on the soot resulting from interactions with these acids.

Publications

Rogaski, C. A., L. R. Williams, and D. M. Golden, Heterogeneous interactions of NO_2, SO_2, O_3, HNO_3 and H_2SO_4 with model soot surfaces, in preparation.

Global and Regional Impacts of Stratosphere-Troposphere Exchange on the Perturbation of the Chemistry by Subsonic Aircraft Emissions

Investigators

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Research Objectives

The research activity we propose in the framework of the 3-D modeling effort is the assessment of the importance of small scale processes affecting the exchange of chemical compounds between the stratosphere and the troposphere, and to provide for the core model an evaluation and, if necessary, a parameterization of these complex dynamical processes. Indeed, an important limitation of the ability of a modeling system to appropriately represent stratosphere-troposphere exchange is the scale dependency of the processes responsible for the exchange.

Also, in the framework of the global modeling initiative, the stratospheric chemistry code developed by Guy Brasseur will be implemented into the 3-D model.

Summary of Progress and Results

- The 3-D chemistry code has been tested and is currently under modification to accommodate the requirements of the modeling group.

- An analysis of the cross-tropopause exchange at the global scale in CCM2 is currently under way. In particular, different methods (conservation of mass and residual circulation) are being compared.

- At the mesoscale level, a collaborative effort between NASA Goddard and NCAR for the study of the PV-budget in a storm simulated by the mesoscale model MM5 using data from NASA DAO is underway.

Publications

None

Effects of Subsonic Aircraft on Aerosols and Cloudiness in the Upper Troposphere and Lower Stratosphere

Investigator

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Research Objectives

Review data obtained during the NASA GASP program and produce a synoptic climatology of aerosol properties, cloudiness, and conditions suitable for contrail formation and persistence, based on that dataset.

Summary of Progress and Results

Due to the fact that most of the first year funds did not arrive on campus until the end of last calendar year, our work is just getting underway. As new students start here in the fall, we will not be able to hire a research assistant for this program until next fall.

A small part of the GASP dataset was obtained from Greg Nastrom at St. Cloud State University. Archived meteorological data in the form of gridded datasets suitable for plotting has been obtained. Software has been written to extract parameters of interest from the GASP data and to plot them for a first look. Software has also been developed to plot aircraft tracks and gridded meteorological data simultaneously. This allows an aircraft observation at a particular time to be assigned to a particular meteorological regime. Preliminary subjective typing of the meteorological regimes along two flight tracks has been done, and observations obtained during those flights have been assigned to the corresponding categories in a database. We are developing ways to automate the building of this database as much as possible. We are building it in such a way that it can be modified and adapted to new analyses as our ideas develop.

We hope to hire a graduate research assistant for this project beginning this fall. We anticipate that the data processing will be semi-automated by that time and that a significant fraction of the GASP data can be processed into a climatology by next spring.

Publications

None

2-D Representation of 3-D Modeling of Atmospheric Effects of Aircraft

Investigators

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Research Objectives

The overall goal of this project is to develop a 2-D model that best represents a 3-D model. The subtasks are as follows:

(1) Compare the GSFC 2-D model using Eulerian and residual-mean dynamics derived from the same 3-D model;

(2) Develop a statistical treatment of convective vertical transports and rain-out from a 3-D model and compare the 2-D model results with a 3-D model using statistics derived from the 3-D model;

(3) Do the same as in (2) for cloud cover effects;

(4) Develop and use a statistical treatment for asymmetries in temperature to use in T-dependent reaction rates;

(5) Using (1) through (4) above, compare the derived 2-D model assessment with that derived from the 3-D model.

Summary of Progress and Results

We are beginning (1) using the GSFC STRATAN dynamics together with the GSFC CTM. No results have been obtained thus far.

Publications

None

Analyses of Aircraft Data for: (1) Providing Evidence of Aviation Effects on the Chemical Composition of the Troposphere, and (2) Establishing Baseline Chemical Data in Remote Regions for Use in Future Assessments

Investigators

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Research Objectives

The objective of the research is to analyze existing NASA GTE and AASE aircraft data bases for purposes of:

(1) Identify for each region of study meteorological scenarios and air-mass sources (trajectory analyses) which were important to the region during the measurement period and establish a chemical composition of tropospheric air for the identified scenario. Where appropriate establish a link between observed chemical composition and meteorology/source-air characteristics.

(2) For each meteorological/source-air scenario defined as being important, to examine on a climatological basis (±2 years) the representativeness of the measured data for that region and scenario.

(3) Where data from the GTE/AASE missions include measurements over periods of years in the same region, to identify any long-term trends in major species (e.g., ozone, CO, nitrogen gases, etc.) and relate to current ideas or trends (literature).

(4) In performing (1) through (3) above, to identify any data from the aircraft data bases which provide clear evidence of the influence of aircraft emissions in the troposphere (e.g., aircraft wake or corridor samples).

Summary of Progress and Results

The ABLE 3A, ABLE 3B, and PEM-A data bases have been edited and compiled into scenarios and chemical datasets formed. Analyses have been performed on ABLE-3A. For ABLE-3A, three scenarios were established as important to the Alaskan region (summertime): marine polar air, Siberian-source continental air, and Canadian-source continental. For ABLE-3B (Canada) data are being compiled into two major classifications and data bases have been formed—air with a 5 day source north of the polar jet and south of the jet. Several sub-sets of air within each are at the present time being examined to determine if sufficient chemical data are available to merit further sub-division. Planned work for the remainder of the year includes compiling the PEM-B and TRACE-A datasets and completion of analyses (with figures and tables) of the ABLE-3A, ABLE-3B, and PEM-A data.

Publications

None

Analysis of 20 Years of Balloon Borne Aerosol Data for Atmospheric Effects of Subsonic Aircraft

Investigator

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Research Objectives

The research objective is to analyze the University of Wyoming aerosol data record, obtained from monthly balloon flights at Laramie since 1971, looking for possible effects of commercial jet aircraft in the 10-12 km region. This will be mainly an analysis of the occurrence of thin layers of condensation nuclei (CN), which are present in jet contrails.

Summary of Progress and Results

The program began with minimal FY94 funding in September 1994. Since then, the PI has investigated CN profiles from balloon flights at Laramie for the summer season since about 1984 (when high resolution, digital data became available). The summer (June, July and August) season is when the natural background of CN is highest due to photochemical production of particles. These data, up to 1990 (the period when the PI was at the University of Wyoming and made the measurements) has been analyzed. Most of the 21 flights analyzed show conspicuous (narrow layers of high concentration) CN layers in the 10-12 km region which likely do not have a natural origin. These layers are suspected to be the remnants of aircraft contrails. Since most of these soundings were made at daybreak, the contrail remnants are probably at least 10-18 hours old. The source of these CN layers can be further analyzed by: 1) examining other seasons in the Laramie data record (in winter the natural CN source is smaller but the aircraft source should be similar), and 2) by examining similar data obtained at McMurdo Station in Antarctica during past austral spring ozone expeditions (aircraft sources of CN should be absent at 10-12 km over Antarctica). In addition, data obtained by the University of Wyoming between 1990 and the present will also be analyzed. We expect to conduct these studies during the next year with the partial help of a post-doctoral associate.

Publications

None

Two-Dimensional Modeling of Subsonic Effects

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Research Objectives

This research project was proposed to help assess the effects of subsonic aircraft with the use of a contemporary two-dimensional (latitude vs. altitude) photochemistry and transport model.

Summary of Progress and Results

We have used our two-dimensional photochemistry and transport model to assess the effects of both subsonic and supersonic aircraft on the atmosphere using scenarios provided by Linda Hunt and Karen Sage at Langley Research Center. The subsonic fleet is predicted to increase yearly average global total ozone by about 0.5%. The maximum increases are in the polar northern hemisphere fall where values are above 1%.

We are collaborating with Professor Marvin Geller and colleagues (State University of New York, Stony Brook) in a study of the representation of the dynamics in our model and how these might be improved, especially in the troposphere and lower stratosphere.

Publications

None

Assessing the Effects of Subsonic Aircraft on Ozone

Investigators

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Research Objectives

- To develop the GISS/Harvard/UCI model into a research tool for analyzing subsonic aircraft effects on tropospheric ozone. Emission inventories, chemical parameterization schemes, deposition algorithms, and compiled atmospheric observations developed for that model will be made available to the AEAP/SASS Science Team.

- To deliver to the Science Team a documented chemical code for tropospheric and stratospheric chemistry, and to maintain this code over the duration of the project.

- To test the representation of atmospheric transport in the SASS core model using simulations of CFCs, ^{85}Kr, ^{222}Rn, ^{210}Pb, excess ^{14}C released in nuclear explosions, and other tracers.

- To evaluate the concentrations of tropospheric ozone, NO_x, NO_y, CO, and hydrocarbons simulated in the Core model with observational statistics from surface, aircraft, balloon, and satellite platforms.

Summary of Progress and Results

- We have developed detailed and comprehensive emission inventories of NO_x, CO, and isoprene for use in global simulations of tropospheric chemistry. We are presently constructing chemical parameterization functions for rapid integration of chemical rates in a tropospheric ozone simulation.

- Preparation of a documented chemical code for the SASS Science Team is on schedule. We have improved the user interface and are writing code documentation. We are also installing in the code a facility for steady state calculations.

- We have been working with D. Koch and K. Turekian (Yale) on a global simulation of ^{7}Be, a radioisotope which could provide a useful test of convective transport in the Core model. We have compiled a data base of input variables and output diagnostics for testing the simulation of transport in global 3-D models with the chemical tracers CFCs, ^{85}Kr, and ^{222}Rn. This data base has already been used by D. Rind at GISS for on-line evaluation of the GISS GCM, and it is freely available to the SASS Science Team.

- We are presently completing a global 3-D model study of CO including exhaustive evaluation of model results with observations.

- We have prepared a climatology of tropospheric ozone, based on ozonesonde data, surface data and estimates of the tropospheric ozone column. This climatology will be made available to the community, as will the sonde data, in a form convenient for model input, or evaluation.

Publications

None

Development of Remote Sensing Techniques for Determination of Contrail Properties from Satellites

Investigators

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Research Objectives

- Quantify capability for automatically detecting contrails from satellites.

- Develop and apply techniques to derive effective particle sizes, optical depths, and heights of clouds using multispectral satellite data both day and night.

- Examine changes in cloudiness induced by contrails.

- Measure cirrus and contrail coverage over the U.S. for different seasons and at different times of day using both Sun-synchronous and geostationary satellites and relate the results to weather and air traffic patterns.

- Initiate the development of a global contrail climatology using Sun-synchronous satellite data and flight track information.

Summary of Progress and Results

- Attended first SASS Science Team meeting in June 1994 and presented results of analyses demonstrating procedures for quantifying contrails from satellites.

- Presented overviews of potential contrail effects on the radiation budget at June 1994 AEAP meeting and at an international air pollution conference in September 1994.

- Developed working relationship with Air Force contrail community and procured 1 year (April 1993 - April 1994) of hourly surface contrail observations from 20 Air Force bases in U.S. as part of climatology and correlative data base. Derived first contrail statistics for potential SASS experiment sites. Most favorable months are April and May.

- Performed first intercomparison of aircraft *in situ* and satellite retrievals of particle sizes in contrails and presented at the "Improving Contrail Forecasting" Workshop at Wright-Patterson Air Force Base, January 12-13, 1995. Good agreement was obtained for the single case study.

- Acquired first installment (1-month) of a 1-km resolution, Sun-synchronous satellite dataset from University of Texas for analysis to compare with Air Force surface observations and continued development of contrail detection and quantification techniques.

- Contributed to SASS Science Plan manuscript as part of SASS Science Panel and worked with SASS lead scientist to help formulate experiment plan.

Publications

Minnis, P., An overview of satellite observations of contrails and their radiative impact on climate, presentation at Atmospheric Effects of Aviation Project Annual Meeting, Virginia Beach, VA, 1994.

Minnis, P., Direct and indirect effects of natural and anthropogenic aerosols on the Earth's radiation budget, aerosols and atmospheric optics: Radiation balance and visual air quality, International Specialty Conference and Courses, Snowbird, UT, 1994.

Background NO$_x$ Concentrations in the Upper Troposphere as a Result of Lightning

Investigators

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Research Objectives

To develop a global climatology of lightning-produced NO$_x$ for comparison with NO$_x$ concentrations emitted from subsonic aircraft.

Summary of Progress and Results

During the past year we have concentrated on two aspects of the research project. One involves developing a global lightning climatology, while the other starts to address the NO$_x$ question by evaluating the amount of energy in a typical lightning flash.

A global lightning climatology has been developed using parameterizations developed by one of the investigators, which utilizes satellite observed cloud climatologies from the ISCCP data base. The ISCCP data base allows the separation of deep convective clouds (thunderstorms) from all other clouds and therefore the regional distribution of lightning sources can be studied. The ISCCP data base supplies more than seven years of data (1983-1990) and therefore monthly climatologies can be constructed using the seven complete years of data. The cloud data are available at 3 hour resolution and therefore some investigation has been carried out into the daily fluctuations of global and regional lightning patterns. The global lightning climatologies will soon be made available to other researchers.

The second area we have progressed in is the study of the detailed physics of individual lightning discharges. We have analyzed lightning data from the National Lightning Detection Network (NLDN) to determined the climatological values of peak current and multiplicity (number of return strokes) that are crucial in understanding how much energy is available to produce NO$_x$. We have used an empirical model of a lightning discharge, together with the above observed parameters to calculate the amount of energy available in an average lightning flash. Toward the same goal we are using observed parameters of the global electric circuit to isolate the contribution of lightning to the global currents that flow through the atmosphere. We hope this method will provide the total integrated energy for the production of NO$_x$ and will compliment the results obtained with the empirical lightning discharge model. Once we have a handle on the energies in the system, we can progress the next step to calculate the amount of NO$_x$ produced per flash.

Publications

Two in progress.

Multiscale Atmospheric Transport Modeling for Subsonic Assessment

Investigators

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Research Objectives

Participate in the development of a core 3-D global chemical transport model for AEAP assessments through the following tasks:

- Continue experiments with the GSFC 3-D advection algorithm to isolate and quantify transport mechanisms relevant to aircraft emissions and operations. Prepare and test a convective transport algorithm in association with this advection scheme in the Goddard CTM. Algorithm to use diagnostic variables output from the Relaxed Arakawa-Schubert convective parameterization in GEOS-1 data assimilation model.

- Evaluate transport in the global CTM convective module using a hierarchy of smaller-scale models (Penn State/NCAR Mesoscale Model (MM5) and Goddard Cumulus Ensemble Model (GCE)). Evaluations to be accomplished through a series of case studies examining redistribution of boundary layer tracers and strat/trop exchange associated with convective events.

- Evaluate in the same manner one additional convective transport algorithm that may be contributed to the core model by another group. Algorithms designed for use with other GCMs (CCM2, GISS, etc.) may be evaluated in a climatological sense using a combination of GCE convective transport statistics and satellite cloud cover observations.

- Deliver the documented GSFC 3-D advection and convection algorithms for use in the core global CTM. Participate in the integration and implementation of these transport modules in the core global CTM.

Summary of Progress and Results

Convective transport algorithm has been developed. Algorithm has been tested in case study of 10-11 June 1985 PRESTORM squall line over Oklahoma/Kansas. CO tracer studies performed in GCE, MM5, and global CTM for this event. CO mixing ratios at anvil level are of similar magnitude in all three simulations. Boundary layer CO mixing ratios remain too large behind storm in global CTM due to lack of downdraft parameterization. Summertime regional monthly average transport out of boundary layer over Central U. S. is well-characterized by GEOS-1 cloud mass fluxes, based on comparisons with combination of GCE and ISCCP statistics.

Publications

Pickering, K. E., A. M. Thompson, W.-K. Tao, R. B. Rood, D. P. McNamara, and A. M. Molod, Vertical transport by convective clouds: Comparisons of three modeling approaches, *Geophys. Res. Lett., 22,* 1089-1092, 1995.

Wang, Y., W.-K. Tao, K. E. Pickering, A. M. Thompson, R. Adler, J. Simpson, P. Keehn, and G. Lai, Mesoscale (MM5) simulations of TRACE-A and PRESTORM convective events, *J. Geophys. Res.,* in press, 1996.

Analysis of *In Situ* Contrail Measurements from FIRE Cirrus IFO-II

Investigator

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Research Objectives

- To document the sizes and types of cloud hydrometeors in contrails in several different environmental conditions.

- To assess which of these situations produce contrails with the most potential for radiative effects.

Summary of Progress and Results

The initial phase of the analysis has focused on the identification of contrail penetrations made with the UND Citation aircraft during the FIRE Cirrus IFO-II in 1991 and the DOE ARM RCS IOP in 1994. The measurements of aerosol concentrations from the condensation nuclei (CN) counter and small ice particles concentrations from the FSSP probe are being combined with flight notes, forward-looking video and flight track information to determine when aircraft exhaust and contrails were sampled. These samples are being grouped as to whether or not contrail clouds were encountered in the exhaust plume and whether the plume was embedded within natural cirrus. Most of the encounters have been with the exhaust of the Citation during course reversal maneuvers, but at least one "foreign" contrail sample has been found.

While at least one embedded contrail has thus far been identified, there were a number of Citation exhaust plumes in natural cirrus which did not apparently form persistent condensation trails. This observation is based on the fact the characteristic signature of contrails, coincident peaks in CN and FSSP concentrations, were absent in these cases. The particle replicator data may shed some light on this phenomenon.

Present activities are focused on a case study comparing several contrails that occurred under clear and cloudy conditions.

Publications

In situ observations of contrail microphysics, presentation at the AEAP Annual Meeting, Virginia Beach, VA, 23-28 April 1995.

The Climatic Impact of Subsonic Aircraft Emissions

Investigators

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Research Objectives

The research objectives are to evaluate the potential climatic impacts of subsonic aircraft emissions, including their effect on water vapor, ozone, atmospheric aerosols, clouds and carbon dioxide.

Summary of Progress and Results

In the first stage of this research, we have concentrated on the effects of water vapor emissions. Water vapor emissions, at the altitude and locations of subsonic aircraft, are input to the GISS Global Climate/Middle Atmosphere model, and their impact on climate is assessed. Water vapor emission rates spanning five orders of magnitude are used to determine the characteristics of the system's response. Results indicate that: 1) effects are highly non-linear with emission rates, due to the saturation properties of the atmosphere; 2) the relative increase in specific humidity and cloud cover maximizes near the altitude of emission (~12 km), while the temperature response maximizes a few km lower; 3) while the relative increase in water vapor shows a tendency to maximize at the latitude of maximum emission (Northern middle latitudes), the absolute increases in water vapor and high level cloud cover occur in the tropics, due to advective processes and differences in water holding capacity; 4) hence the surface air temperature and high altitude temperature responses are relatively uniform with latitude, and also do not maximize at the latitudes of maximum emissions. In comparison with the doubled CO_2 climate simulation, the temperature and cloud cover response as a function of latitude and altitude are roughly similar, the relative specific humidity increase peaks at the same altitude but, in the doubled CO_2 case, it peaks in the tropics (rather than in the northern extratropics). These conclusions imply that the relative specific humidity increase in the upper troposphere might be the best climatic "footprint" from aircraft-level water vapor emissions, while the feedbacks of the system dominate the forcing in most other respects. A paper describing these results is being prepared for publication.

In addition, to this specific study, we are pursuing the more general objective of trying to understand the relation between radiative forcings at the tropopause and the resulting climate change at the Earth's surface. We are preparing two papers, one developing an efficient climate model for these studies, and a second which uses this model for a general comparison of the effectiveness of each of these potential forcings. The first paper is completed. The second will be ready by June 1995 and they will submitted at the same time to *Journal of Geophysical Research*.

Publications

Hansen, J. E., R. Ruedy, G. Russell, J. Lerner, M. Sato, A. Lacis, and D. H. Rind, Wonderland climate model, submitted to *J. Geophys. Res.*, 1995.

Hansen, J. E., M. Sato, and R. Ruedy, Radiative forcing experiments, in preparation, 1995.

Rind, D. H., P. Lonergan, and K. Shah, The climate impact of water vapor emissions at the altitude and location of subsonic aircraft, in preparation, 1995.

Model Assessment of the Impact of Ozone on Subsonic Aircraft

Investigators

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Research Objectives

The objectives of the proposed work are as follows:

- To coordinate the efforts of the Science Team which will develop, evaluate, and analyze a three-dimensional chemical-transport model to be used by AEAP in the assessment of the impact of supersonic and subsonic aircraft. This effort will be coordinated by Dr. Jose M. Rodriguez, who will act as Project Scientist;

- To simulate the chemistry of aircraft plumes, and the impact of these subgrid process on the representation of aircraft emissions in large-scale models;

- To develop a parameterization of different chemical schemes which will allow efficient and accurate computation of the chemistry in the 3-D CTM;

- To develop diagnostics useful to interpret the results of 2-D assessment calculations, and interface with diagnostics from 3-D models; and

- To continue utilizing our 2-D CTM to provide assessment results as required by the program.

Summary of Progress and Results

Funding through the end of 1994 was used to accomplish tasks associated with the first of these goals. Dr. J. M. Rodriguez worked with the team at Lawrence Livermore National Laboratory and AEAP Program Scientists to:

- Convene a meeting of modelers to discuss the proposed modeling approach; this meeting took place in Washington, DC, 12-14 June 1995.

- Finalize Science Team composition and coordinate with team members revised statement of work in accordance with the adopted modeling philosophy.

- Organize and lead first meeting of the Science Team in Pleasanton, CA, 12-14 December 1994.

- Prepare draft of project description document, to appear as a chapter in the SASS first program report.

Publications

None

Investigations of Tropical-Middle Latitude Exchange in the Upper Troposphere and Lower Stratosphere

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Research Objectives

The purpose of this work is to investigate the dynamical processes which transport mass between the tropics and the middle latitudes in the upper troposphere and lower stratosphere and the degree to which these can be correctly diagnosed in global analyses which serve as the input to these transport models. Three-dimensional chemical transport models will be an essential tool in assessing the impact of subsonic aircraft on the atmosphere, and it thus important that horizontal transport near the tropopause is modeled correctly. Our goal is to assess the accuracy of trajectories of air parcels traveling between the tropics and middle latitudes near the tropopause. In the research, we are focusing on trajectories from the global analyses that can be validated with data from aircraft field campaigns and other tracer data.

Summary of Progress and Results

Research began this fiscal year (1995). The work to date has followed two complementary tracks; the first of these is the task of developing a trajectory code to run on computers located on-site at Ames, and the second is to perform diagnostic analyses of case studies for trajectory modeling. The first task will not be completed until the SGI Indigo2 workstation recently acquired by Dr. Pfister has been fully loaded with software to support the Schoeberl trajectory program. This will be completed by the end of April 1995. Once this is completed, we will perform a series of comparison studies with a transport model developed by Drs. Richard Young and Howard Houben of NASA/Ames. In the interim we have been running limited tests using the Goddard machines over the network.

Diagnostic work is currently in progress on a number of case studies from the ASHOE/MAESA transit flights. During the March 1993 flights in particular, the tracer data (e.g. N_2O and NO_y) from the ER-2 show a remarkably sharp transition in the between middle latitude and tropical air deep in the tropics south of Hawaii. We are investigating the evolution of this transition or boundary in the Goddard assimilation model (ASM) analyses. In a large-scale sense, the ASM analyses correctly show an upper tropospheric jet displaced southward during the March flight campaign which has the effect of tightening gradients at these levels and above. This is in broad agreement with the tracer data. Trajectory analyses currently underway will be used to identify the origins of parcels on either side of the tropical/mid-latitude transition in the tracer data.

Publications

None

Improvement of Jet Stream Wind Analyses Using Commercial Aircraft Data

Investigators

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Research Objectives

- Obtain an additional 4000 daily wind and temperature readings from data sparse regions using commercial aircraft flight data recorders.

- Compare these data against the output from the Goddard Earth Observing System (GEOS-1) and operational analyses.

- Utilize the additional readings to improve the accuracy of the GEOS-1 analyses.

Summary of Progress and Results

During the first half-year of this project, we have modified the on-board flight data recorder programs and obtained the first samples of high resolution aircraft data from all British Airways 747-400 aircraft. Protocols and security features are currently being negotiated to permit this data to be transmitted to SUNY and NASA Goddard over the Internet. Professor Leonid Rukhovets has joined the research group to work on the data utilization portion of the experiment.

Publications

Tenenbaum, J., Jet stream wind analyses: Comparisons of aircraft observations with analyses and gravity wave parameterizations, submitted to *Wea. and Forecasting*, 1995.

Regional-Scale Impacts of Aircraft Emissions

Investigators

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Research Objectives

- Test and calibrate a convective parameterization using simulations of conditionally unstable environments with the Goddard cumulus ensemble model. Emphasis will be on defining microphysical and dynamic parameters necessary for accurately simulating vertical redistribution of heat and moisture within convective mixing algorithm. Results would be extended to chemical tracer redistribution.

- Implement an evaluated/refined convective venting algorithm for describing convective-induced tendencies in heat, moisture, and trace chemical constituents within AEAP models.

- Simulate the short-term chemical fate of aircraft exhaust using our regional-scale tropospheric chemistry model (formerly RADM) during spring and/or summer simulation periods.

- Extract and evaluate the dry and wet deposition algorithms from our regional-scale tropospheric chemistry model. Provide these subroutines to related AEAP programs that need calculations of scavenging rates of dry deposition velocities.

- Use upper tropospheric trajectory model to simulate the multi-day chemical fate of individual aircraft exhaust parcels.

- Parallel with the Lagrangian parcel chemical simulations, a state-of-the-science sensitivity and uncertainty analysis will be applied to calculated ozone formation/destruction rates resulting from aircraft emissions. Key reactions and species that contribute to uncertainties in model calculations will be identified.

Summary of Progress and Results

This new project has been funded for eight months. We have prepared a Lagrangian parcel model for simulating the chemical fate aircraft exhaust for periods of up to a week or more. We have performed initial comparisons between lower and upper tropospheric chemical processes that occur as emitted NO_x and organic compounds are oxidized into secondary pollutants, and have quantified rates of ozone formation as the parcel is chemically oxidized for various NO_x emission rates. Preliminary sensitivity studies of the Stockwell chemical mechanism have identified key reactions and species that may contribute to uncertainties in the rates at which ozone is formed in the lower and upper troposphere.

Publications

Walcek, C. J., and J. Schwab, Factors influencing the vertical distribution of tropospheric HNO_3, NO_x, and other reactive nitrogen compounds, submitted to *Geophys. Res. Lett.*, 1995.

Radiative Effects of Subsonic Jet Contrails

Investigators

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Research Objectives

- To utilize the spectral characteristics of the AVHRR sensor and develop a robust and automated technique to identify jet contrails.

- To utilize the multi-channel HIRS data in order to examine the conditions necessary for contrail formation.

- To determine the radiative forcing of subsonic jet contrails by using the ERBE data.

Summary of Progress and Results

A large number of AVHRR images have been manually examined for contrails, in order to produce a good working dataset for further research. Several images with a variety of contrails were found. These images include examples of contrails over land, water, clouds, etc. Detecting contrails in AVHRR imagery is not always an easy task, even for trained human observers.

The automated detection scheme of Engelstad *et al.* [1992] has been completely implemented. This technique computes a contrail-enhanced image from the difference between AVHRR channels 4 and 5, applies a ridge detection scheme, and then uses the Hough transform to detect straight line segments corresponding to jet contrails. The method appears to work quite well on the majority of contrail images.

Investigations into other detection schemes are also in progress. One promising method is a new iterative technique for ridge detection. A local 3x3 ridge template is used to detect thin linear features; then the image is thinned by gray-scale morphological erosion, and the process is repeated. Each iteration detects ridges of slightly greater thickness. After just one or two iterations, thin linear features such as jet contrails are dramatically enhanced.

This scheme has the advantage of detecting linear features, even when they do not form a straight line segment. It may even obviate the need for applying the Hough transform, which would increase the detection speed significantly. Further work is necessary to compare the speed and accuracy of this technique to the Engelstad method.

The AVHRR channels 1 and 3 are being used to determine the optical depth and particle size of contrails. These microphysical properties of contrails will then be compared to those of the naturally occurring cirrus around the contrails in order to examine the possibility of using these signatures to distinguish between contrails and cirrus clouds.

Publications

Christopher, S. A., J. M. Weiss, and R. M. Welch, Towards an automated approach for detecting jet contrails using AVHRR data, presentation at Atmospheric Effects of Aviation Project Annual Meeting, Virginia Beach, VA, 1995.

Engelstad, M., T. Lee, S. K. Sengupta, and R. M. Welch, Automated detection of jet contrails using the AVHRR split window, *Int'l. J. Remote Sens.*, *13*, 1391-1412, 1992.

Analyses of Scenarios for Past and Possible Future Aircraft Emissions

Investigator

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Research Objectives

Tasks to be done under several components. These include: continuing as chair of the Emissions Scenarios Committee for AEAP; coordinating with the International Civil Aviation Organization (ICAO) to ensure the highest quality possible in the emissions scenarios promoted by the Emissions Scenarios committee; continuing as member of Emissions Inventories Subgroup (EISG) under ICAO towards international analysis of aircraft emissions inventories; performing analyses to compare and evaluate databases of aircraft emissions developed for NASA and by various international groups and from these analyses, develop guidelines for future emissions scenarios development; and performing sensitivity analyses, using our 2-D chemical-transport model of the global troposphere and stratosphere, to determine potential sensitivity of further enhancements that could be made to emissions scenarios development. The latter studies will be used in prioritizing further emissions scenario development.

Summary of Progress and Results

Although this is a new project, a number of activities were accomplished in 1994 at LLNL before my move to Illinois and several new activities are in progress. With my old group at LLNL, I have continued development of 2-D and 3-D chemical-transport models for use in aircraft studies, and have applied these models to sensitivity analyses of aircraft effects. Model calculations were also included in the WMO/UNEP international ozone assessment. In the 3-D model, we have done a preliminary study of soot emissions, and are proceeding with a more complete sensitivity analysis in the 2-D model. The effects of operational assumptions for NO_x and other emissions are currently being evaluated in the 2-D model.

Several meetings of the Emissions Scenarios Committee were held in the last year, and I am continuing to coordinate activities with NASA, Boeing, and McDonnell Douglas towards validation of existing scenarios and development of new scenarios to meet aircraft assessment needs.

Several meeting have been held of the Emissions Inventory Subgroup (EISG) of ICAO. Analyses are in progress to compare the NASA-developed emissions database with European developed databases. I am also contributing to preparation of a document for ICAO on findings of the EISG.

Publications

Kinnison, D. E., H. S. Johnston, and D. J. Wuebbles, Model study of atmospheric transport using carbon 14 and strontium 90 as inert tracers, *J. Geophys. Res.*, *99*, 20647-20664, 1994.

Li, L., T. R. Nathan, and D. J. Wuebbles, Topographically forced planetary wave breaking in the stratosphere, submitted to *Geophys. Res. Lett.*, 1995.

An Airborne Investigation of Aircraft Aerosol Emissions and Wake/Plume Characteristics

Investigators

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Research Objectives

We proposed an airborne study to investigate, as a function of meteorology and flight conditions for a variety of commercial-class aircraft, the 1) emission ratio (relative to fuel burned), size distribution, volatility, and growth rate of aircraft generated particulate; 2) the geometry, flow fields, thermal dissipation rates, dispersion rates, and efficiency of exhaust trapping of/within aircraft wake vortices; and 3) the physical characteristics of contrails. The strategy of this program was to instrument a lightweight, jet aircraft—the NASA Wallops Flight Facility (WFF) T-39E—with a compact payload of trace gas, aerosol, and turbulence sensors and obtain measurements downstream of NASA and U. S. Air Force airline-category jets engaged in other projects/flight maneuvers. Data would be collected over a wide range of aircraft separation distances (e.g., plume age) for a variety of meteorological and flight scenarios (e.g., during climb and at cruise), both within the troposphere and lower stratosphere. These measurements address two key elements of the Subsonic Assessment (SASS) Program (e.g., Near-Field Interactions and Plume Mixing/Dispersion plus Engine Exhaust Characterization) and are essential for parameterizing and validating the aircraft wake/plume and climate impact models used/developed under this program.

Summary of Progress and Results

Although this project was not officially accepted for funding until 16 March 1995, significant progress has been made toward project goals:

- Procurement of critical instruments and sensors not available at LaRC has been initiated; delivery of these items are expected in the April/May time frame.

- A collaboration has been established with Al Viggiano of Air Force Phillips Laboratory for provision of mass spectral measurements of important reactive trace gases aboard the T-39 during the aircraft emission study. The investigators have visited Phillips Lab twice to work out details of modifying the mass spectral instrument to fit within the T-39, developing an efficient reactive gas sampling inlet, and developing schemes for calibrating and validating the mass spectral measurements.

- The investigators have designed 2 inlets--one for aerosol measurements and the other for mass spectral measurements of reactive trace gases--and an aerosol collection system which will be constructed by Wallops and used aboard the T-39 for airborne sampling. We were aided in the designs by LaRC aeronautical engineers and are having the designs reviewed and approved by the LaRC flight safety board before construction and deployment aboard the aircraft. This process should be completed by 31 March; flight tests of the completed inlets and collectors are scheduled for late April.

- The investigators have had several meetings with Wallops Flight Facility staff regarding aircraft modification and flight planning. As a result, Wallops personnel have or are currently 1) adding hard points and pilons to the T-39 wings to facilitate mounting optical scattering aerosol probes; 2) drilling holes in the aircraft's radome to allow installation of the differential pressure measurement

system which is used for atmospheric turbulence and air flow measurements; 3) installing stiffening plates at strategic places within the aircraft cabin to allow mounting of external sensors and inlets; 4) mounting temperature, pressure, and Lyman Alpha sensors on the airframe; and 5) developing plans for flight tests and field measurements.

- Condensation nuclei and aerosol scattering instruments selected for use in the field program are being calibrated in our laboratory under anticipated field conditions using in-house aerosol generation equipment.

- Instrument racks were obtained from Wallops and are being prepared (wired/plumbed) for use in the upcoming field program.

We anticipate that critical preparations will be completed in time to allow a brief field experiment from Wallops during the late June/early July time period. Our plan is to fly within the wake of a NASA T-38 aircraft at cruise altitude and at separation distances ranging from a few hundred meters out to 100 km. These initial measurements will focus on determining the aircraft's emission ratios of soot and sulfate particles and how these change as a function of time and also how the concentration of reactive gases (H_2SO_4 and HNO_3) change with plume age. Secondary objectives will be to determine whether all exhaust effluents are trapped within the wing vortices and to examine the geometry of the trailing vortices at various distances behind the source aircraft in order to acquire data for validating aircraft wake/plume models.

Additional project objectives will be pursued in flights conducted in the fall of 1995 and the spring of 1996. Current plans call for deployment of the T-39 during the April 1996, SASS-sponsored SUCCESS mission to facilitate an intercomparison of species measurements common between it and the NASA DC-8, and to provide information on exhaust near-field conditions as the DC-8 investigates far-field effects.

Publications

Results of the summer 1995 field experiment will be submitted to *Geophysical Research Letters* in late 1995 and will be reported in oral presentations in mid-1996.

Particulate Characterization of Commercial Jet Engine Emissions at Cruise: (1) in Near Field Exhaust Plumes and (2) in the North Atlantic Corridor

Investigators

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Research Objectives

- To provide particulate characterization in the near field of the exhaust plumes of commercial transports operating at cruise.

- To provide particulate characterization during a study of the North Atlantic Flight Corridor as collaborators in the EEC project POLINAT.

Summary of Progress and Results

Work started on these objectives in August 1994 in preparation for the POLINAT winter campaign scheduled for 1-12 November 1994. The MASS, one airborne sub-unit and one ground-based sub-unit were shipped to Munich, Germany and Shannon, Eire respectively, following pre-flight calibration in Rolla. Measurements were made in the corridor before, during and after the corridor was established each campaign flight day. Data on total CN concentration, size distribution and emission indices for particulate emissions were recorded. Also, several special missions were flown to interrogate the plumes of specific commercial transports and similar data were acquired. Preliminary data evaluations look excellent. The POLINAT team meets on 21-22 March 1995 at MPI Heidelberg for a workshop to discuss all the data and modeling to date, and to plan for the scheduled summer campaigns in July 1995. Detailed analysis of all the data from the winter campaign should be available to the research community following the workshop in March 1995.

Publications

Hagen, D. E., P. D. Whitefield, and M. B. Trueblood, Particulate characterization in the near field of commercial transport aircraft exhaust plumes using the UMR-MASS, Part 1, submitted to *J. Geophys. Res.*, 1994.

Hagen, D. E., P. D. Whitefield, and M. B. Trueblood, Particulate characterization in the near field of commercial transport aircraft exhaust plumes using the UMR-MASS, in *Conference Proceedings: Impact of Emissions from Aircraft and Spacecraft upon the Atmosphere*, U. Schumann and D. Wurzel, Editors, German Aerospace Research Establishment (DLR), Cologne, Germany, 1994.

Whitefield, P. D., D. E. Hagen, and J. Paladino, Upper tropospheric SO_2 pollution and condensation nuclei formation: Evidence from aircraft measurements over the North Atlantic, submitted to *Geophys. Res. Lett.*, 1994.

The Role of Turbulent Mixing in the Chemistry and Dispersion of the Wake of Subsonic Aircraft

Investigators

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Research Objectives

The goal of this research, initiated in July 1994, is to gain a better understanding of the role of turbulent mixing on the dispersion and chemistry of the wakes of subsonic aircraft flying in the neighborhood of the tropopause and to provide valid subgrid parameterizations of this effect for the larger scale climate models needed to assess the environmental impact of the projected fleet of subsonic aircraft. We are utilizing numerical Large-Eddy Simulations (LES) of the turbulence to represent mixing during the period from several seconds to almost an hour after wake generation.

Summary of Progress and Results

Part of the initial effort on this project was devoted to making modifications to our existing code, previously used for simulations of atmospheric turbulence in marine clouds. These have included: 1) the capability for variable grid in both horizontal directions; 2) modifications to accept initial conditions appropriate for the wake several seconds behind an aircraft; and 3) generation of some turbulent-wave fields appropriate for ambient atmospheric conditions in the neighborhood of the tropopause.

A number of simulations of wake dispersion have been made. The mutual interactions of the vortices, after perturbation by the atmospheric motions, lead to quite distinctive breakup eddies. Comparisons show our simulation results to have qualitatively similar features to those seen in photographs of wakes we have taken. We are in the process of investigating the sensitivity of the dispersion in this breakup region to initial vortex pair parameters, which depend upon aircraft variables, and to atmospheric variables such as stratification, turbulence, and wind shear.

We observe strong fluctuations in species concentrations and temperature in the vortex breakup region which may be expected to have an influence on chemical processes in the wake. This will be studied in the future as we continue our investigation of the role of turbulent mixing on the dispersion and chemistry of the wakes of subsonic aircraft flying in the neighborhood of the tropopause.

We made a presentation of our program plans at the Near-Field Interactions meeting 22-23 August 1994, and made a visit to Continuum Dynamics, Inc. in January to coordinate our wake modeling efforts.

Publications

None

Modeling Macro- and Micro-Scale Turbulent Mixing and Chemistry in Engine Exhaust Plumes

Investigators

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Research Objectives

The primary research objective of this study is to understand the effects of micro-scale turbulent mixing and chemical processes in an engine jet plume. The evolution of the plume in the near field and the subsequent interaction of the jet plume with the large scale entrainment processes such as those caused by the aircraft wingtip vortices is being studied using a new numerical/analytical method.

Summary of Progress and Results

To assess the potential impact of the aircraft exhaust products on the atmosphere a numerical study is underway to characterize the chemical and mixing processes that occur in the jet plume. Two issues are being currently investigated: 1) how the chemical processes (including heterogeneous reactions due to condensation of exhaust water vapor) affect the overall ozone concentration when the jet plume is directly interacting with the ambient air, and 2) how the above noted chemical processes are modified when the plume begins to interact with the aircraft's wingtip vortices. In the near field, a study has been carried out using a previously developed chemical kinetics and a new 10-step reduced mechanism. Two numerical methods are being used: a well-mixed-reactor model which assumes that all species are perfectly mixed, and a probability density function (pdf) Monte Carlo simulation model that accounts for some imperfect mixing effects in the jet plume. The results show that the new reduced mechanism predicts (with significantly reduced computational cost) the ozone response to within 10% of the prediction using the full mechanism. The maximum ozone decrease predicted using the well-mixed reactor is about -0.35% which is not too different from earlier predictions of -0.5 to -0.1% obtained using a "box" model (Danilin *et al.*, 1994). However, the pdf simulations predict a much smaller ozone response with a maximum value of -0.1% suggesting clearly that mixing time-scales are important. Since mixing is altered considerably when the plume interacts with a wingtip vortex, another study is underway using a large-eddy simulation (LES) method to model the interaction between two longitudinal vortices that are initially separated by prespecified distance. Full 3-D Navier-Stokes equations supplemented by scalar equations that act as tracers for the species in the plume vortex and the ambient wingtip vortex are solved in a time and space accurate manner. Preliminary results show that due to mutual induction, the two vortices rotate around each other and eventually merge in a complex manner. The ambient turbulence plays a major role in exciting the azimuthal instability in the vortices and this in turn enhances the vortex breakdown and entrainment process.

Publications

Menon, S., and J.-Y. Chen, A numerical study of mixing and chemical processes during interactions between an aircraft's engine jet plume and its wingtip vortices, presentation at Atmospheric Effects of Aviation Annual Meeting, Virginia Beach, VA, 1995.

Modeling Condensation and Chemistry in the Exhaust Plumes and Vortex Wake of Subsonic Air Transports

Investigators

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Research Objectives

Numerical models of the condensation, chemistry and fluid mechanics occurring in the exhaust plumes and vortex wakes of aircraft will be enhanced and extended to include the phenomena relevant to subsonic air transports. The physical and chemical processes that need to be modeled include: 1) the fluid dynamical processes driving the mixing, 2) the chemical evolution of the emissions (through both homogeneous gas-phase reactions and aerosol-mediated chemistry), and 3) the condensation behavior of the mixture. The plume and wake modeling will build on work done in HSRP/AESA using SPF2 as the plume code and UNIWAKE for the wake regime. The current effort will enhance the condensation models and refine the chemistry to include tropospheric and generally lower altitude flight conditions appropriate to the subsonic fleet. NCAR flight data using an instrumented Sabreliner 60 to probe the exhaust of a Learjet 35 will be compared with predictions to test and evaluate the model. Specific comparisons will be made for wake vortex scale lengths and magnitudes, particle diffusion in the plume, contrail formation and particle growth, and thermal/moisture structure within the plume. Data comparison experience gained with the NCAR data will be used in interpreting other data made available from European measurement programs or other measurements under AESA and/or SASS sponsorship.

Summary of Progress and Results

Candidate subsonic aircraft for plume and wake calculations have been identified using AEAP scenarios and currently available flight measurements. Aircraft configuration data and engine data has been sought for these airplanes, including the Learjet 35. For the Learjet wake measurements, the data have been reviewed and specific datasets are being analyzed to extract quantities for comparison with wake calculational results. Additional numerical studies of coagulation phenomena in the plume have been begun. These near-field calculations have focused on interactions between homogeneously mediated H_2SO_4/H_2O embryos and exhaust soot particulates. Based on these results, initial estimates for the amount of emitted soot that are active CCN are currently being formulated. Subsequent work will use these estimates to model diffusional growth of contrail particles under various ambient conditions.

Publications

None

SAGE II Aerosol, Cloud, Water Vapor, and Ozone Observations in Subsonic Aircraft Flight Corridors

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Research Objectives

Analyze the SAGE II data base for the presence of statistically significant perturbations in aerosols, cloud frequencies, water vapor, or ozone at flight altitudes in established subsonic flight corridors.

Summary of Progress and Results

The locations of subsonic flight corridors have been defined by the aircraft emissions database developed by Boeing and McDonnell Douglas and available from the Upper Atmosphere Data Program database at NASA Langley. The number of SAGE II observations inside and outside these corridors has been established, and the seasonal variations of aerosol extinction at 1.02 micron and ozone concentration have been studied. In order to investigate possible connections between the observed aerosol and ozone differences and meteorological conditions, seasonal variations of temperature, tropopause height, tropopause pressure, and tropopause temperature inside and outside the corridors have also been studied.

It was found that at high latitudes, the number of SAGE II observations inside and outside the corridors are comparable, but at low latitudes, the number of observations per season outside the corridors is much higher than the number of observations inside the corridors. At low latitudes, aerosol extinction values inside flight corridors are slightly higher than those outside flight corridors, but at high latitudes, the reverse is true. Similar differences are also observed for ozone concentration. It is also observed that at low latitudes, tropopause heights inside flight corridors are generally lower than those outside flight corridors, but the reverse is true at high latitudes. In general, temperatures inside flight corridors are lower than temperatures outside flight corridors. Detailed analyses of aerosols and trace gases inside and outside the flight corridors for each month are planned when monthly aircraft emission data become available.

Publications

None

Appendix C

Acronyms

APPENDIX C

ACRONYMS AND ABBREVIATIONS

1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional
AASE II	Second Airborne Arctic Stratospheric Experiment
ABLE 3A	Arctic Boundary Layer Expedition 3A
ABLE 3B	Arctic Boundary Layer Expedition 3B
A/C	aircraft
ACE	Aerosol Characterization Experiment
ACMAP	Atmospheric Chemistry Modeling and Analysis Program
AEAP	Atmospheric Effects of Aviation Project
AEDC	Arnold Engineering Development Center
AER	Atmospheric and Environmental Research, Inc.
AERONOX	Impact of NO_x Emissions from Aircraft upon the Atmosphere
AES	Atmospheric Environment Service (Canada)
AESA	Atmospheric Effects of Stratospheric Aircraft
AFOSR	Air Force Office of Scientific Research
AGU	American Geophysical Union
AIAA	American Institute of Aeronautics and Astronautics, Inc.
ALIAS	Aircraft Laser Infrared Absorption Spectrometer
ANCAT	Abatement of Nuisance caused by Air Traffic
APIPs	Aircraft-produced ice particles
ARC	Ames Research Center
ARI	Aerodyne Research, Inc.
ARM	Atmospheric Radiation Measurement
ARMCART	Atmospheric Radiation Measurement/Clouds and Radiation Testbed
ASHOE/MAESA	Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft
ASM	Goddard Assimilation Model
ASTP	Advanced Subsonic Technology Program
ATMOS	Atmospheric Trace Molecule Spectroscopy
AVHRR	Advanced Very High Resolution Radiometer
CAEP	Committee on Aviation Environmental Protection
CAMED	University of Cambridge/University of Edinburgh
CART	Clouds and Radiation Testbed
CASSCF	complete-active-space self-consistent-field
CCM2	Community Climate Model-2
CCN	cloud condensation nuclei

CFC	chlorofluorocarbon
CFD	computational fluid dynamics
CIAP	Climatic Impact Assessment Program
CIMS	Chemical Ionization Mass Spectrometer
CIRES	Cooperative Institute for Research in Environmental Studies
CITE	Chemical Instrumentation Test and Evaluation
CN	condensation nuclei
CRT	chemical radiative transport
CSU	Colorado State University
CTM	chemical transport model
DAAC	Distributed Active Archive Center
DAO	Data Assimilation Office
DIAL	differential absorption lidar
DLR	Deutsche Luft Raumfahrt (German Aerospace Research Establishment, Germany)
DOE	Department of Energy
EAC	electric aerosol classifier
ECMWF	European Center for Medium Range Weather Forecast - UK
EEC	European Economic Community
EETC	Engine Exhaust Trace Chemistry
EG/TG	emitted gas divided by total gas
EI	emission index
EISG	Emissions Inventory Subgroup
ELCHEM	Electrified Cloud Chemistry
EM	electron microscopy
EOSDIS	EOS Data and Information System
EPA	Environmental Protection Agency
ERBE	Earth Radiation Budget Experiment
ETOPS	extended twin-engine operations
FAA	Federal Aviation Administration
FARS	Facility for Atmospheric Remote Sensing
FIRE	First ISCCP Regional Experiment
FSSP	Forward Scattering Spectrometer Probe
FTIR	Fourier Transform Infrared
FY	Fiscal Year
GASP	Global Atmospheric Sampling Program
GC	gas chromatography
GCE	Goddard Cumulus Ensemble
GCM	general circulation model
GC/MS	gas chromatograph/mass spectrometer
GEAE	General Electric Aircraft Engines
GEOS-1	Goddard Earth Observing System Data Assimilation System, Version 1

GFDL	Geophysical Fluid Dynamics Laboratory
GISS	Goddard Institute for Space Studies
GMI	Global Modeling Initiative
GPS	global position system
GSFC	Goddard Space Flight Center
GTE	Global Tropospheric Experiment
HC	hydrocarbon
HIRS	High Resolution Infrared Radiation Sounder
HIS	High spectral resolution radiometers
HPFE	High Pressure Flow-Tube Experiment
HSCT	high-speed civil transport
HSRP	High-Speed Research Program
Hz	hertz
ICAO	International Civil Aviation Organization
IFO	Intensive Field Observations
IGAC	International Global Atmospheric Chemistry Programme
IMPACT	Integrated Massively Parallel Atmospheric Chemistry Model
IN	ice nuclei
INS	inertial navigation system
INSTAC	International Stratospheric Air Chemistry Campaign
IOP	Intensive Operation Period
IPCC	Intergovernmental Panel on Climate Change
IR	infrared
ISCCP	International Satellite Cloud Climatology Project
IUPAC	International Union of Pure and Applied Chemistry
IWC	ice water content
JGR	Journal of Geophysical Research
JPL	Jet Propulsion Laboratory
LaRC	Langley Research Center
LAS	laser aerosol spectrometer
LDI	lean, direct injection
LeRC	Lewis Research Center
LES	Large-Eddy Simulations
LIF	laser-induced fluorescence
LIRAD	combined lidar and radiometry technique
LLNL	Lawrence Livermore National Laboratory
LPP	lean, prevaporized, premixed

MASS	Mobile Aerosol Sampling System
MIT	Massachusetts Institute of Technology
MLOPEX	Mauna Loa Observatory Photochemistry Experiment
MM	Mesoscale Model
MMS	Meteorological Measurement System
MODIS	Moderate-Resolution Imaging Spectrometer
MPIC	Max-Planck Institute for Chemistry
MRCI	Multireference configuration-interaction
MTP	Microwave Temperature Profiler
MTPE	Mission to Planet Earth
NARE	North Atlantic Regional Experiment
NASA	National Aeronautics and Space Administration
NAT	nitric acid trihydrate
NCAR	National Center for Atmospheric Research
NDIR	non-dispersive infrared
NFI	Near-Field Interaction
NIST	National Institute of Standards and Technology
NLDN	National Lightning Detection Network
NMC	National Meteorological Center
NMHC	nonmethane hydrocarbon
NMUHC	nonmethane unburned hydrocarbons
NOAA	National Oceanic and Atmospheric Administration
NOAA/AL	NOAA Aeronomy Laboratory
NOAA/CMDL	NOAA Climate Monitoring and Diagnostics Laboratory
NRA	NASA Research Announcement
NRC	National Research Council
NSF	National Science Foundation
OAG	Offical Airline Guide
ONERA	Office National d'Études et Recherches Aerospatiales
OSLO	University of Oslo
OTA	Office of Technology Assessment
P_3	combustor inlet pressure
PALMS	Particle Analysis by Laser Mass Spectrometry
PAN	peroxyacetyl nitrate
pdf	probability density function
PEM	Pacific Exploratory Mission
PEM-T	Pacific Exploratory Mission - Tropics
PEM-West	Pacific Exploratory Mission - West
PI	Principal Investigator
PLIF	planar laser-induced fluorescence
PMS	particle measurement system
POLARIS	Photochemistry of Ozone Loss in the Arctic Region in Summer
POLINAT	Pollution from Aircraft Emissions in the North Atlantic Flight Corridor

PRESTORM	Preliminary Regional Experiment for STORM-Central
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
PSC	polar stratospheric cloud
PV	potential vorticity
P&W	Pratt & Whitney

RADM	Regional Acid Deposition Model
RCS	Remote Cloud Sensing
RH	relative humidity
RMS	Root mean square
RQL	rich-quench-lean
RRKM Theory	Theory developed by Rice, Ramsperger, Kassel, and Marcus regarding how association reactions (A+B->AB) occur

SAGE II	Stratospheric Aerosol and Gas Experiment II
SASS	Subsonic Assessment
SLS	Stratospheric Limb Sounder
SNIF	SASS Near-Field Interaction Flight Experiment
SOS/SONIA	Southern Oxidants Study/Southeast Oxidants and Nitrogen Intensive Analysis
SPADE	Stratospheric Photochemistry, Aerosols and Dynamics Expedition
SRI	SRI International
SSA	Stratospheric sulfate aerosols
STE	stratospheric-tropospheric exchange
STERAO	Stratosphere, Troposphere Experiments: Radiation, Aerosols, Ozone
STRAT	Stratospheric Tracers of Atmospheric Transport
STRATAN	Stratospheric Analysis by Data Assimilation
STRATOZ	Stratospheric Ozone Expedition
STREAM	Stratosphere and Troposphere Experiments by Aircraft Measurements
SUCCESS	Subsonic Aircraft: Contrail and Cloud Effects Special Study
SUNY	State University of New York

T$_3$	combustor inlet temperature
TANS	Trimble Advanced Navigation System
TDL	tunable diode laser
THC	total hydrocarbon
TOGA COARE	Tropical Ocean Global Atmosphere/Coupled Ocean Atmosphere Response Experiment
TOTE/VOTE	Tropical Ozone Transport Experiment/Vortex Ozone Transport Experiment
TRACE-A	Transport and Atmospheric Chemistry near the Equator - Atlantic

| UARP | Upper Atmosphere Research Program |
| UARS | Upper Atmosphere Research Satellite |

UAV	unmanned aerial vehicle
UCI	University of California at Irvine
UCLA	University of California at Los Angeles
UMR	University of Missouri, Rolla
UN	United Nations
UND	University of North Dakota
UNEP	United Nations Environmental Programme
USAF	United States Air Force
UT/LS	upper troposphere/lower stratosphere
UTRC	United Technologies Research Center
UV	ultraviolet
VET	vibrational energy transfer
VPFR	Variable Pressure Flow Reactor
WFF	Wallops Flight Facility
WINDTEMP	Boeing computer code and database of climatological winds and temperatures on world air routes
WMO	World Meteorological Organization
wt%	weight percent

Appendix D

Chemical Formulae and Nomenclature

APPENDIX D

CHEMICAL FORMULAE AND NOMENCLATURE

Be	beryllium
^{6}Be	beryllium-6
^{7}Be	beryllium-7
BrO	bromine monoxide
^{14}C	carbon-14
C_n	generic designation for species with n carbon atoms
C_2H_2	acetylene
C_2H_4	ethylene
C_2H_6	ethane
C_2H_4O	ethanal (acetaldehyde)
C_2H_5CHO	propionaldehyde
$C_2H_5O_2H$	ethyl hydroperoxide
C_2H_5ONO	ethyl nitrite
$C_2H_5ONO_2$	ethyl nitrate
$C_2H_5O_2NO_2$	ethyl pernitrate
C_3H_6	cyclopropane, propylene
C_3H_6O	propanal
I-C_3H_7ONO	isopropyl (2-propyl) nitrite
n-C_3H_7ONO	normal propyl (1-propyl) nitrite
I-$C_3H_7ONO_2$	isopropyl nitrate
n-$C_3H_7ONO_2$	normal propyl nitrate
I-$C_3H_7O_2NO_2$	isopropyl pernitrate
n-$C_3H_7O_2NO_2$	normal propyl pernitrate
C_3H_8	propane
C_4H_8O	butanal
$C_4H_9ONO_2$	butyl nitrate
C_4H_{10}	butane
$C_5H_{10}O$	pentanal
$C_5H_{11}ONO_2$	pentyl nitrate
C_5H_{12}	pentane
C_6H_{14}	n-hexane
C_7H_{16}	n-heptane
CCl_4	carbon tetrachloride
CF_4	perfluoromethane
CFC	chlorofluorocarbon
CFC-11	$CFCl_3$
CFC-12	CF_2Cl_2
CFC-113	CCl_2FCClF_2

CFC-115	$CClF_2CF_2$
CH_2O	formaldehyde (methanal)
CH_2CH_2	ethene (ethylene)
CH_2CHCH_3	propene
CH_3	methyl radical
CH_3Br	methyl bromide

CH_2CHO
CH_2CO } radicals from ethene oxidation
CH_2OH

CH_3CCl_3	methyl chloroform
$CH_3C(O)OO$	acetyl peroxy radical
CH_3CHO	acetaldehyde (ethanal)

$CH3CH(OH)CH_2O$
$CH_3CH(OO)CH_2CH_2CH_3$
$(CH_3)_2CHO$ } radicals from acetaldehyde oxidation
CH_3CO

CH_3COCHO	methyl glyoxal

CH_3COCH_2
$CH3COCH_2O$
$CH_3COCH_2O_2$
$CH_3COCH_2O_2NO_2$ } radicals and recombination products from methyl glyoxal
CH_3COCH_2ONO oxidation
$CH_3COCH_2ONO_2$
CH_3COCH_2OOH

CH_3COO_2	peroxyacetyl radical
$CH_3COO_2NO_2$	peroxyacetyl nitrate (PAN)
CH_3COCH_3	acetone
$CH_3C(O)OONO_2$	peroxyacetyl nitrate (PAN)
CH_3O	methoxy radical
CH_3O_2	methyl peroxy radical
CH_3O_2H	methyl hydroperoxide
CH_3ONO	methyl nitrite
CH_3ONO_2	methyl nitrate
$CH_3O_2NO_2$	methyl pernitrate
CH_3OOH	methyl peroxide
CH_4	methane
Cl_y	inorganic chlorine
ClO	chlorine monoxide
Cl_2O	dichlorine monoxide
$ClONO_2$	chlorine nitrate
C_nH_{2n}	generic alkene
$C_nH_{2n}O$	generic aldehyde or ketone
C_nH_{2n+2}	generic alkane

C_nH_{2n+1}
$C_nH_{2n+1}O$ } radicals from alkane oxidation
$C_nH_{2n+1}O_2$

$C_nH_{2n+1}OOH$	generic peroxide
$C_nH_{2n+1}ONO$	alkyl nitrite
$C_nH_{2n+1}ONO_2$	alkyl nitrate
$C_nH_{2n+1}O_2NO_2$	alkyl pernitrate
CO	carbon monoxide
CO_2	carbon dioxide
H	atomic hydrogen
Halon-1301	CF_3Br
HC	hydrocarbon
HCFC-141b	$CFCl_2CH_3$
HCHO	formaldehyde (methanal)
HCl	hydrogen chloride
HNO_2	nitrous acid
HNO_3	nitric acid
HNO_4	peroxynitric acid
HO_2	hydroperoxy radical
HO_x	hydrogen oxide
H_2O	water
H_2O_2	hydrogen peroxide
HOCl	hypochlorous acid
C_nH_{2n}	generic alkene
HOC_nH_{2n}	
$HOC_nH_{2n}O$	
$HOC_nH_{2n-1}O$	
$HOC_nH_{2n}O_2$	
$HOC_nH_{2n}ONO$	radicals and recombination products from alkene oxidation
$HOC_nH_{2n}ONO_2$	
$HOC_nH_{2n}O_2NO$	
$HOC_nH_{2n}O_2NO_2$	
HONO	nitrous acid
HO_2NO_2	peroxynitric acid
H_2SO_4	sulfuric acid
^{85}Kr	krypton-85
M	unreactive gaseous species participating in termolecular reactions through its ability to quench excited intermediates (typically oxygen or nitrogen)
NAD	nitric acid dihydrate
NAT	nitric acid trihydrate
NH_4HSO_4	ammonium bisulfate
$(NH_4)_2SO_4$	diammonium sulfate
NMHC	nonmethane hydrocarbon
NMUHC	nonmethane unburned hydrocarbons

NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxide
NO_y	reactive nitrogen (= $NO + NO_2 + HNO_3 + 2N_2O_5 + ClONO_2 + HO_2NO_2 + PAN + ...,$)
N_2O	nitrous oxide
N_2O_5	dinitrogen pentoxide
O	atomic oxygen
$O(^1D)$	atomic oxygen (first excited state)
O_2	molecular oxygen
O_3	ozone
OH	hydroxyl radical
ORG	generic designation for an organic
PAN	peroxyacetyl nitrate
^{210}Pb	radioactive isotope of lead
R'	organic radical fragment
^{222}Rn	radon-222
RO	alkoxy radicals
RO_2	organic peroxy radical
RONO	alkyl nitrite
$RONO_2$	alkyl nitrates
RO_2NO_2	organic pernitrate
SF_6	sulfur hexafluoride
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_x	sulfur oxide
soot	A particulate product of incomplete combustion with the empirical formula C_nH_n
THC	total hydrocarbon

Appendix E

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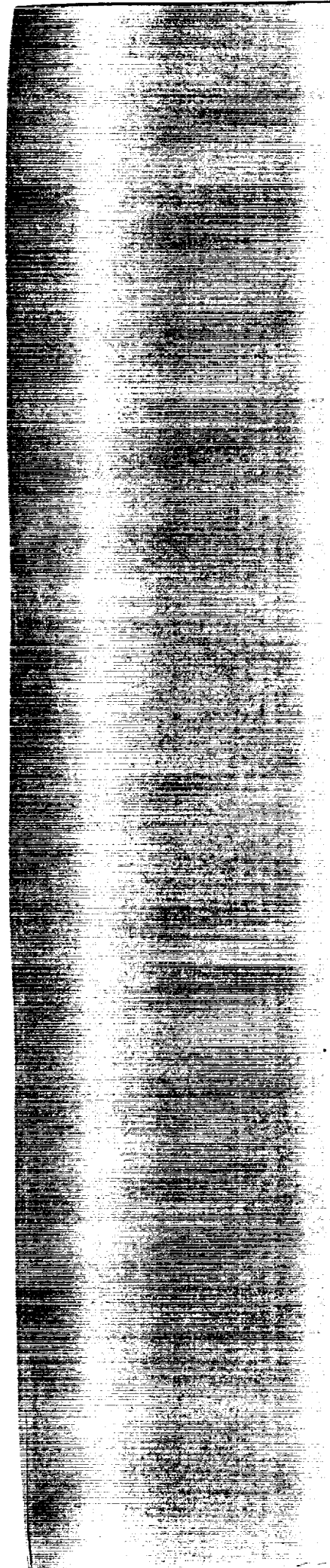Greenbelt Road
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REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE May 1996	3. REPORT TYPE AND DATES COVERED Reference Publication

4. TITLE AND SUBTITLE

Atmospheric Effects of Aviation: First Report of the Subsonic Assessment Project

5. FUNDING NUMBERS

C-538-08-12
Code 910

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS (ES)

Office of Aeronautics and Space Administration
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8. PEFORMING ORGANIZATION REPORT NUMBER

96B00080

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS (ES)

National Aeronautics and Space Administration
Washington, DC 20546-0001

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

NASA RP-1385

11. SUPPLEMENTARY NOTES

Thompson: Goddard Space Flight Center, Greenbelt, Maryland; Friedl: Office of Mission to Planet Earth, HQ, NASA, Washington, D. C.; Wesoky: Office of Aeronautics, HQ, NASA, Washington, D. C.

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Unclassified - Unlimited
  Subject Category 45

Availability: NASA CASI (301) 621-0390.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This document is the first report from the Office of Aeronautics Advanced Subsonic Technology (AST) Program's Subsonic Assessment (SASS) Project. This effort, initiated in late 1993, has as its objective the assessment of the atmospheric effects of the current and predicted future aviation fleet. The two areas of impact are ozone (stratospheric and tropospheric) and radiative forcing. These are driven, respectively, by possible perturbations from aircraft emissions of NO_x and soot and/or sulfur-containing particles. The report presents the major questions to which project assessments will be directed (Introduction) and the status of six programmatic elements: Emissions Scenarios, Exhaust Characterization, Near-Field Interactions, Kinetics and Laboratory Studies, Global Modeling, and Atmospheric Observations (field studies).

14. SUBJECT TERMS

Stratospheric chemistry, tropospheric chemistry, aerosols, ozone, subsonic fleet, aircraft emissions, upper troposphere, lower stratosphere, cirrus, contrails.

15. NUMBER OF PAGES
330

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

National Aeronautics and
Space Administration

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